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CHAPTER X.

THE RELATIONS OF METAMORPHISM TO STRATIGRAPHY.

INTRODUCTORY.

It is sufficiently evident from the previous chapter that rocks which have very similar lithological characters may have had very different origins. This point can probably best be appreciated with the aid of a few illustrations.

(a) It is well known that often it is difficult or impossible to discriminate limestones of organic and chemical origin.

(b) Sometimes true water-deposited conglomerates and volcanic tuffs closely resemble each other, and often they grade into each other. This last occurs wherever volcanoes are adjacent to the sea and the fragmental material falls partly upon the land and partly in the water.

(c) A disintegrated and partly decomposed granite or other massive rock in situ is often very similar to an arkose which is formed from it. For instance, it has been pointed out that the arkoses which are forming in the Gulf of California are practically identical in mineral and chemical character with the rocks from which they are formed. In western United States at various places, even where there is very little alteration, in the field it is difficult to delimit sharply the massive rocks, such as granite, from the arkoses built up from and resting upon them.

(d) It is frequently difficult to determine whether igneous rocks are tuffs or are lavas broken during flowage. Gradations between these two classes of rocks occur where tuffaceous material falls upon unconsolidated lavas.

If rocks comparatively little modified and of different origin may so closely resemble one another that they are difficult to discriminate, it is plain that after profound metamorphism they may be still nearer alike. In

fact, in many cases rocks of diverse origins have become so similar that as yet no criteria have been devised by which they can be discriminated from one another.

It has been fully explained that many of the minerals produced by metamorphic processes are the same as those produced by crystallization from a magma and have identical characters. It has further been seen that during metamorphism secondary textures and structures are formed in rocks of all kinds. Some of the secondary textures are enlargement, cataclastic, laminated, porphyritic. Some of the secondary structures are jointing, faulting, bedding partings, cleavage, fissility, schistosity, gneissosity. At the time these textures and structures are produced the original textures and structures are usually obscured, and they are not infrequently obliterated. And even if the original textures and structures are not greatly modified they are often overlooked because of the prominence of the secondary textures and structures.

Finally, where rocks of different origin but similar chemical composition are strongly metamorphosed with the production of secondary textures and structures, it is scarcely possible to discriminate them, for, as has been fully shown, upon the original chemical composition of the rocks and upon the conditions of their alterations depends the character of the resultant product. Two metamorphosed rocks of different origin but similar chemical composition may have practically identical mineralogical, textural, and structural characters.

DISCRIMINATION BETWEEN METAMORPHOSED SEDIMENTARY AND METAMORPHOSED IGNEOUS ROCKS.

For the purposes of stratigraphy, it is very desirable that, so far as possible, the criteria be given by which metamorphosed sedimentary rocks may be discriminated from metamorphosed igneous rocks. So long as the sedimentary rocks retain little modified clastic textures, either macroscopical or microscopical, they can be discriminated as such. So long as the igneous rocks retain the igneous textures, these may readily be recognized in thin sections. Also, it has been fully explained on pages 644–645, 689–690, that, in so far as the alterations are those of mass-static conditions, the textures and structures are not rapidly destroyed, so that it is ordinarily easy to recognize with the microscope the original textures of such rocks, even if complete

recrystallization has taken place. A very good illustration of this is the ready recognition of the aporhyolites as volcanic rocks by the presence of spherulitic and other igneous textures. Further, it has been pointed out that where the conditions are mass-mechanical for rocks in the zone of fracture, they are merely broken up into blocks or slices and that the textures in the integral masses are preserved. Therefore, the origin of rocks altered under mass-mechanical conditions in the zone of fracture may usually be determined. Stated in another way, one may say that when the alterations are of a kind to which the prefix *apo* is applicable, under the significance given to it on pages 776–777, it is easy to discriminate between altered igneous and altered sedimentary rocks.

In contrast with the above, it has been explained that where the rocks are mashed in the zone of anamorphism previous textures and structures are rapidly destroyed. This may go so far as to obliterate not only the textures and minor structures, but even the major structures of the sedimentary and igneous rocks, such as bedding and differentiation. Naturally there are all grades of this process of destruction. It is only when the mashing has gone so far as to have granulated and recrystallized the rocks in the zone of anamorphism, and has thereby transformed them to schists or gneisses, that original textures and structures are wholly destroyed.

CASES OF CONFUSION.

The following are some of the classes of igneous and sedimentary rocks which are most likely to be confused:

(1) The schistose and gneissic sedimentary rocks are particularly likely to be confused with the schistose and gneissic tuffs. Both classes of these rocks in their original form may have a lamination or banding which is roughly similar; and if the alterations go far enough to destroy the textures, the rocks frequently assume a very similar aspect.

(2) Metamorphosed sedimentary rocks derived from arkoses and graywackes—i. e., derived from material in which the original minerals have been but little sorted—are likely to be with difficulty discriminated from metamorphosed igneous rocks. This follows, first, from the fact that the chemical composition of such rocks does not necessarily vary from that of some igneous rocks; and, second, from the fact that arkoses and graywackes are frequently very coarsely banded or even massive, so that the

sediments have somewhat the same homogeneity of structure that igneous rocks possess. Where there is any considerable sorting of the sedimentary materials, so that they are arranged in layers of different composition, this fact tends to prevent their change to forms which appear similar or identical with metamorphosed igneous rocks.

(3) A third case which has occasioned difficulty is that of an igneous rock which has been intruded by another igneous rock in a very complicated fashion, so that the intrusive contains very many fragments of the intruded rock. These fragments are oftentimes partly absorbed, and thus take on a pseudo-conglomeratic aspect. While it is comparatively easy in most cases to separate such a rock from a true conglomerate when in the unalterated condition, the difficulty of the discrimination increases in proportion as the metamorphism is advanced. The difficulty may be appreciated from the fact that cases are known where unmetamorphosed pseudo-conglomerates of intrusion and true conglomerates which happen to be side by side have been confused by geologists. In various cases included blocks in gneissoid granites have been taken as evidence of the sedimentary character of these rocks. This mistake has been made in reference to the Cottonwood granite of the Wasatch, which contains rounded fragments, or else segregations in situ, which have distinctly the aspects of bowlders. Similar phenomena have led to like conclusions in the Lake Superior region. In some instances the intruded rock and included blocks are schist. In such cases parallel injections are also likely to occur. Thus we have a pseudo-conglomerate, below which are alternating layers of different kinds. These phenomena in the Lake Superior region have led certain geologists to the conclusion that the explanation of the phenomena is downward progressive metamorphism; but it has been shown that the phenomena are due to intrusion. These difficulties are greatly increased where the rocks have been mashed subsequent to the intrusions.

(4) Another case in which it may be difficult to determine the origin of the metamorphosed rocks is that of the porphyritic schists. By the mashing of a porphyritic igneous rock the matrix may become schistose. The phenocrysts may become rounded by the interior movement, and closely resemble residual fragmental material. In many cases the porphyritic schists of sedimentary origin are derived from material which contains large grains or crystals in a fine-grained matrix. The matrix may be

recrystallized and the larger particles, being more resistant, only flattened. Thus schists derived from porphyritic igneous rocks and from sediments containing materials of varying coarseness may closely resemble each other.

Another way in which close resemblance between porphyritic schists of sedimentary and of igneous origin may arise is the development of porphyritic constituents during metamorphism. The new porphyritic minerals may show random orientation if formed under mass-static conditions, or parallel orientation if formed under conditions of mashing. The augen-gneisses are cases of this kind. For instance, the augen of one gneiss may be the partly mashed original porphyritic feldspars of an igneous rock, while those of another gneiss may be newly developed porphyritic constituents in a metamorphosed sediment. In such cases it is difficult or impossible to determine from the appearance of the rock whether an augen-gneiss is of igneous or of sedimentary origin.

(5) After igneous rocks have been deformed in the zone of fracture the openings may be filled by cementation. Subsequent mashing may break the fillings into fragments, and shearing may give them roundish forms which very closely simulate pebbles. This happens in more instances with quartz veins than with other minerals. Such metamorphosed schists bear numerous apparent pebbles of quartz, and are very difficult indeed to discriminate from metamorphosed sedimentary rocks which contain true waterworn pebbles of quartz.

(6) A final class of cases in which it is very difficult to determine what part of a rock mass is igneous and what part is sedimentary is that in which a sedimentary rock has been injected in a complicated fashion by one or more igneous rocks, and later the combined mass is metamorphosed. Such a schist is derived partly from a sedimentary and partly from an igneous rock. Some cases are as follows:

A metamorphosed fissile sedimentary rock, such as mica-schist or mica-gneiss, may be injected in a complicated way parallel to the schistosity, and thus produce a banded gneiss, part of which is igneous and part sedimentary. The rock may be predominantly of either one of these materials. If the injected sedimentary rock be subsequently folded, this will produce differential movements parallel to the banding, and the igneous and aqueous bands may be merged into one another and have structures so similar that it is impossible to determine what part of the rock is igneous and what part

aqueous. The Hudson schists and gneisses of southeastern New York, especially near Long Island Sound, are a perfect illustration of rocks produced by the extreme metamorphism of a pelite and the subsequent parallel and cross injection of granitic material.

Another case is that in which an intrusive rock enters a fractured sedimentary rock in such a manner as to give the intrusive masses roundish forms. When later metamorphosed the roundish forms are dissevered, and they may resemble bowlders. The frequent inference is that the rock is a metamorphosed conglomerate, whereas it is a metamorphosed sediment in which the pseudo-bowlders are introduced igneous material.

From the foregoing it is clear that an inseparable schist or gneiss formation may be produced from altered intrusive rocks, from altered lavas, from altered tuffs, from altered sediments, and from any possible combination of two or more of these. Doubtless in many regions in which the schists and gneisses are of a very complex character a number of the processes mentioned in the previous pages, and possibly others unknown, must be united in order to explain all of the phenomena.

While similar schists or gneisses may be derived from sedimentary rocks or from igneous rocks, or partly from each, one who has had much experience in the field is apt to have a bias toward the one or the other origin in a particular instance. But if a given schist or gneiss formation can at no place be traced into a form characteristic either of a sedimentary rock or of an igneous rock, it is extremely hazardous to make positive assertions as to its origin.

CRITERIA FOR DISCRIMINATION.

While the schistose igneous rocks may have foliations, bandings, and lithological characters which very closely simulate those of metamorphosed sedimentary rocks, it is still true of the rocks belonging to the Algonkian and later periods that in many districts the majority of the metamorphosed igneous rocks can be discriminated from the metamorphosed sedimentary rocks.

The more important criteria for discrimination between the metamorphosed sedimentary and igneous rocks are as follows:

(1) The much-mashed igneous rocks are apt to have a very regular, fine foliation and great uniformity of lithological character. If an igneous

mass gradually varies in composition in its different parts, as is so often the case with differentiated magmas, the mashed varieties grade into one another. The complete absence of minor plications, indicating the absence of a parallel structure before the schistosity was produced, is most striking. It is therefore concluded that the finely, regularly laminated, homogeneous schists are usually of igneous origin. It should perhaps be remarked that this is a reversal of the interpretation frequently made at the present time, and which was almost universally made a few years ago.

The converse proposition, that the banded and heterogeneous schists and gneisses are of sedimentary origin, can not be made; for the igneous rocks, intrusive and extrusive, in a given area may have had an original banded character, or may have had great complexity in their parts, as a result of which their mashed equivalents show a banding. This is particularly likely to be true of lavas and tuffs, and may be true even for intrusive masses. Further, it has been seen that the mashed, originally homogeneous, igneous rocks may have become cleaved or fissile, and that along the secondary structure impregnations or injections may occur and the rock thus become banded. If a new mashing now takes place which develops a tertiary structure cutting the secondary one, the minor plications of the secondary structure may simulate similar plications of sedimentary strata.

(2) The metamorphosed sedimentary rocks are not usually so changed as to obliterate all evidence of their original condition. This is true even of the metamorphosed pelites. Minute variations in the coarseness of the laminæ are usually sufficient to produce minor plications which somewhere will be found to intersect the secondary structure. Moreover, in a larger way, thick pelite formations are apt to contain some beds of grit, sandstone, or limestone. These give schists of different kinds, and each of these is different from the metamorphosed mudstone.

Variations in original lithological character are still more prominent when great formations are considered. It has been seen that a sandstone formation may be transformed into a quartz-schist or a micaceous quartz-schist. Limestone may be transformed into marble, bearing greater or less quantities of silicates, depending largely upon its original purity. The arkoses and shales may be transformed into schists and gneisses. Widely disseminated graphite and the presence of ferruginous beds have been regarded as indicating a sedimentary origin. There is no evidence

that any transformations through which sedimentary rocks go are sufficient to obliterate the original differences in thick formations of greatly varying lithological character.

These principles are well illustrated by the Paleozoic metamorphosed sedimentary rocks of the Green Mountains of New England. In this area the Paleozoic rocks have almost completely lost all interior evidence of clastic characters. It is only very rarely, where the rocks were conglomeratic, that any particles can be recognized as fragmental. However, the shales and grits are transformed to mica-schists and mica-gneisses, the sandstones to quartz-schists, and the limestones to marbles. The schists are not evenly homogeneous and regularly schistose with a secondary structure in a single direction, as is so characteristic of metamorphosed igneous rocks. Each formation is composed of minor beds, these beds of minor laminæ. Notwithstanding the metamorphism, these retain to a greater or less degree their integrity. At many places the bedded structures intersect the secondary schistose structures. In a larger way the relations of the formations to one another are those of sedimentary rather than igneous rocks. No one skilled in work in the metamorphic rocks would fail to recognize this Paleozoic series as of sedimentary origin. For the most part these formations can be discriminated from the pre-Paleozoic gneissoid granites.

In regions of extreme metamorphism, where both igneous and aqueous rocks have had long and complex histories, including the development of secondary and perhaps tertiary structures, and sometimes impregnations and injections, no criterion as to texture or minor plication or regular banding is sufficient to discriminate the two. Even in regions in which the great formations may indicate with a high degree of probability that a considerable portion of the material is of sedimentary origin, it may be true that another considerable portion is igneous and can not be discriminated from the aqueous part of the series.

(3) A third criterion of great importance in the discrimination of metamorphosed sedimentary and igneous rocks is chemical composition. It has been shown on pages 555–558 that the materials for sedimentary rocks are sorted, that in general there is depletion in certain of the elements as compared with the igneous rocks, and that the proportions of the elements in the sedimentary rocks are therefore different from those in the igneous

rocks. Furthermore, it has been shown that in the zone of anamorphism the chemical composition of rocks is not greatly changed during the process of metamorphism, and it has already been seen that this is the only zone in which metamorphism is likely to result in the confusion of the two classes of rocks. Therefore the metamorphosed sedimentary and igneous rocks which are likely to be confused have the compositions which are characteristic of their class: the metamorphosed sedimentary rocks, with minor modifications, have the chemical composition of muds, grits, sandstones, etc.; the metamorphosed igneous rocks have the compositions of granites, diorites, etc. For both sedimentary and igneous rocks there are wide variations in chemical composition, but in general the proportions of the elements are markedly different, in the two classes, as may be seen by comparison of the composition of the metamorphosed sedimentary rocks and that of the metamorphosed igneous rocks. The criterion has great value in some cases where the criterion of banding fails, for instance, in discriminating between metamorphosed sedimentary rocks and metamorphosed tuffs. The metamorphosed sediments have their characteristic compositions, while the metamorphosed tuffs, notwithstanding the fact that they may show banding, and thus closely resemble metamorphosed sediments, have the composition of igneous rocks. This criterion has been successfully used by Adams in discriminating between the Grenville gneisses of the Original Laurentian area and the lower granitoid gneiss. The former have the composition, as he has shown, of pelites, whereas the lower gneisses have the composition of granites.

While this criterion of chemical composition is one of the most important and has a wide application, it is not infallible. It has already been seen on pages 497, 870–874 that in such places as the Gulf of California, and certain other localities, the sediments are little decomposed or sorted, and thus there is produced a sedimentary rock which has essentially the same composition as the original igneous rocks from which it was derived.

(4) Closely connected with (3), in fact dependent upon it, is a fourth criterion, that of mineral composition. On account of the difference in chemical composition which has already been mentioned, when the rocks are metamorphosed there results different mineral compositions. It has been seen that the depletion of certain elements in the sediments and the sorting of the material produce comparatively few kinds of original

mechanical sediments. The alterations of these sediments have already been traced out, and it has been seen that from them the common characteristic rocks produced are quartzites, quartz-schists, mica-schists, and mica-gneisses, which are occasionally more or less pyroxenic or amphibolitic, but with these latter materials there is apt to be a considerable quantity of calcareous material. Also, staurolite and andalusite, sillimanite and cyanite are very characteristic minerals. Therefore, where certain single minerals are dominant in the schists and gneisses it seems to be a fairly safe conclusion that the rocks are sedimentary in origin. Thus, where great rock formations are composed chiefly of quartz, chiefly of calcite or other carbonate, or, with these, silicates which may readily develop by the process of silication, it is comparatively safe to assume that the materials from which the schists are derived are of sedimentary origin. Also, schists composed almost wholly of mica and quartz are likely to be of sedimentary origin.

Just as there are mineral combinations which are generally characteristic of sedimentary rocks, so there are others which are generally characteristic of the igneous rocks. From the tuffs and other rocks which develop structures similar to those in the metamorphosed sediments, and are therefore likely to be mistaken for metamorphosed sedimentary rocks, hornblende is likely to develop instead of biotite and muscovite, and thus hornblende-schists and hornblende-gneisses are produced from the metamorphism of the tuffs instead of mica-schists and mica-gneisses. In the igneous rocks with the hornblende, feldspar is apt to be abundantly present, and frequently this feldspar may be near the orthosilicate end of the series. In such rocks, also, there is likely to be present a considerable quantity of titanium, which passes into menaccanite, leucoxene, or titanite. In the igneous schists and gneisses there is likely also to be formed large amounts of epidote and zoisite. The prominence of the various minerals mentioned is due to the fact that the igneous rocks have not been depleted in alkalies and alkaline earths.

But it can not be positively asserted that a metamorphic rock containing metamorphic minerals especially characteristic of igneous rocks may not be of sedimentary origin, for, as already noted, sediments exceptionally contain the unsorted constituents of the original igneous rocks.

In discriminating between the metamorphosed sedimentary and meta-

morphosed igneous rocks it is plain that all the criteria above mentioned should be applied. But where there are intricate mixtures of metamorphosed igneous and sedimentary rocks, as a result of injection, all these criteria may fail to a greater or less extent, for the rocks are not wholly sedimentary or igneous, but a combination of the two.

It is therefore clear that there is frequently very great difficulty in determining the origin of the schists and gneisses, and that the criteria which are at present available are inadequate. However, it is believed that a close study of the character of the changes in each of the well-recognized igneous and sedimentary rocks will in the future furnish other important guides which may be used to discriminate between the two great classes of metamorphosed rocks.

RELATIONS OF METAMORPHIC SEDIMENTARY ROCKS TO STRATIGRAPHY.

VARIATION IN METAMORPHISM.

In working out the stratigraphy of a metamorphosed region the fact that the metamorphism varies in degree under different conditions is of the utmost importance.

UPON WHAT VARIATIONS ARE DEPENDENT.

The variation in the amount and kind of metamorphism is dependent upon many factors (see pp. 39–44), but from the point of view of structure it is necessary to consider only variations depending upon the amount of orogenic movement, upon the character of the rock, and upon the depth of burying.

That the degree of metamorphism is largely dependent upon orogenic movement has been sufficiently shown on previous pages.

It has been seen on pages 760–762 that where rocks consist of alternate layers of different character, these are slow to be obliterated, and especially is this so if the formations be thick. To illustrate, it may be said that it is very difficult, and perhaps impossible, to completely destroy a great limestone or quartzite formation by metamorphism. Also, coarse and strong sedimentary formations are likely to retain their original features to a recognizable degree unless the metamorphism be extreme. The existence of such formations enables one to determine the sedimentary character of

the rocks and often the true strike and dip. In a metamorphosed series the contacts between formations of different character are the most reliable criteria for correct structural observations.

It has been explained (Chapter IV, p. 187) that a formation in the zone of katamorphism is merely fractured, instead of being mashed throughout, and therefore if rocks are deformed under conditions of moderate burying it is usually easy to determine the origin of the rocks with which one is dealing. However, where rocks are deformed at a small depth, faulting is likely to occur, and thus while the problem of stratigraphy is made easier, in that the formations are not so greatly altered, it is made more difficult in that faulting is always a possibility which has to be taken into account.

Rocks which were deeply buried when deformed are mashed, and therefore under these conditions the profoundest kind of metamorphism occurs and all the difficulties which result from extreme metamorphism are introduced. On the other hand, where mashing is the typical kind of deformation faulting is not likely to occur. But it is to be remembered that a series which is mashed before it reaches the surface must pass through the upper zone, and during this passage may again be subjected to dynamic movements and thus be broken and faulted. Consequently, combined with extreme metamorphism we may have also displacement, and in such cases the difficulties of stratigraphy are at a maximum.

RESULTING VARIATIONS.

In handling the various difficulties in stratigraphy which result from metamorphism the variations in amount and kind are of great assistance. Such changes in the nature of metamorphism are to be considered both (1) along the strike, and (2) across the strike.

(1) A series or formation which is profoundly metamorphosed in one part of a district or region may be but slightly metamorphosed in another part. The change in metamorphism is likely to be gradual along the strike. Consequently, by following a formation along the strike, one may solve the problem of the origin of completely metamorphosed formations, for somewhere he may find a locality where it is so little metamorphosed that its original character may be determined. In the less altered area the true succession may be made out, and thus it may be possible to interpret an

extremely metamorphosed district or area by connecting it with areas which are less metamorphosed.

These principles are well illustrated at various places. The Penokee series of the Lake Superior region is very little metamorphosed in the eastern part, but is much more metamorphosed in the western part. A still more striking illustration is found in the Marquette district. In the eastern and central part of the district the rocks are so little metamorphosed that there is no difficulty whatever in determining the origin of the formations. But in the western part of the district, especially in the closely mashed Republic tongue, the three unconformable series there existing—the Archean, the Lower Huronian, and the Upper Huronian—are so mashed and metamorphosed as to appear completely conformable, and one might conclude that here is an inseparable series. However, by tracing the formations along the strike until they connect with the less metamorphosed portions in the central and eastern parts of the district, one is certain that in this tongue there exist three unconformable series.

A third excellent illustration of the change of metamorphism along the strike is furnished by the Ocoee series, which in its northeastern part, in east Tennessee, is but semimetamorphosed, and there it is easy to recognize the original character of the formations. As these formations are traced to the southwest they become more and more metamorphosed, until they are schists and gneisses, and then it is difficult to discriminate between the sedimentary and igneous parts of the series and to separate the Ocoee series from the older series unconformably below.

(2) Rapid change in metamorphism across the strike is frequently as characteristic as is gradual change along the strike. Of course in some cases the change across the strike is gradual, but in many cases it is very abrupt. Thus the rocks on the crown of an arch or at the bottom of a trough may be only partly metamorphosed, while the same formations on the limbs of the folds may be profoundly metamorphosed. This is due to difference in the amount of shearing in different parts of the folds.[a] In other cases the abrupt change in amount of metamorphism is due to the fact that orogenic movement may die out rapidly across the strike or change in its character. As a consequence, rocks on a hill may be folded

[a] Van Hise, C. R., Principles of North American pre-Cambrian geology: Sixteenth Ann. Rept. U. S. Geol. Survey, pt. 1, 1896, pp. 598–600.

and in the next valley be unfolded. They may be very closely folded in a valley and on the mountain beyond be in a horizontal position. The rocks exposed may be strongly metamorphosed by mashing in a mountain mass, because deeply buried during the movement, and along the adjacent area merely be fractured, because in the zone of katamorphism during the movement. Since the amount and kind of metamorphism are so directly a function of the deformation and the depth, the rocks where greatly deformed or deeply buried may be profoundly metamorphosed, and those which are little deformed or near the surface may be comparatively little altered. Failure to understand these principles has led to many mistakes in stratigraphy. Some illustrations of the rapid change across the strike, and of the mistakes in stratigraphy which have resulted, are as follows:

(a) The Taconic Mountains are immediately adjacent, across the strike, to the Hudson River series of New York and Connecticut. The latter formations are little metamorphosed. The rocks in the Taconic Mountains are schists and gneisses. It was therefore concluded by Emmons and by others that the rocks of the Taconic Mountains were metamorphosed before the Hudson River rocks were deposited, and are therefore much older. Hence Emmons gave the Taconic rocks the name Taconic series. The entire Taconic controversy, which has cut such a figure in America, arose from this mistake. It was only when Dana, followed by Pumpelly and those who worked with him, appreciated that there might be very rapid changes in metamorphism across the strike that it was ascertained that the unmetamorphosed Hudson River rocks immediately to the west of the completely metamorphosed schists and gneisses of Greylock and the other Taconic Mountains are parts of the same sedimentary formations.

(b) Another region which very well illustrates the rapid change in metamorphism across the strike is that of the Great Valley and the Unaka Mountains, in the southern Appalachians. The Unaka Mountains are largely composed of the Ocoee series, which is of lower Paleozoic age, and which in the southern part of the region is completely metamorphosed. The metamorphism is much greater than in the rocks of the Great Valley immediately adjacent, also Paleozoic. In the southern part of the region the much metamorphosed Ocoee is thrust over the little altered rocks of the Great Valley.

It is plain from the foregoing that a series of rocks may be profoundly metamorphosed locally and that its metamorphism in an adjacent area may be unimportant. Not only is this so, but different parts of the same fold are often metamorphosed differently, depending upon their positions within the fold. Still further, one set of beds may be more readily metamorphosed than another, so that one formation may be a perfect schist while the adjacent formation may still be plainly fragmental; for instance, a shale may be changed to a mica-schist and an interbedded quartzite be but little affected by any process except cementation. As pegmatization is so frequently dependent upon the presence of an intrusive rock, an extreme phase of metamorphism engendered by volcanism, combined with other processes, may have a very local character.

Notwithstanding the variations of metamorphism, the amount and character of the metamorphism of a series of formations may be an important guide in structural work. It may serve to separate one series from another and assist in determining the structure within a series. The criterion has limitations, which are readily deducible from the facts as to the variation in metamorphism just considered. But if a set of formations be superimposed upon another set and the lower has become schistose throughout, while the upper shows little or no change, it is probable that the lower series underwent a period of metamorphism before the upper series was deposited. In order to make this conclusion at all certain, however, the superior formations should be of kinds which are equally likely to be metamorphosed, further faulting must be excluded, and it must be certain that it is a case of superposition, for laterally the metamorphosing forces may die out rapidly and the altered rocks pass quickly into those but little changed. Still further, if the metamorphism be due to pegmatization as a consequence of the intrusion of great batholiths, the process may die out rapidly in a vertical direction, so that the extremely metamorphosed lower formations gradually pass into the unmetamorphosed beds higher up, with no structural break. Also, it has been seen that metamorphism is a direct function of depth of burying. But probably the change in metamorphism as a result of varying depth of burial is so slow that it ordinarily involves no practical difficulty in separating series.

RELATIONS OF IGNEOUS ROCKS TO STRATIGRAPHY.

Before considering the relations of igneous rocks to stratigraphy it is necessary to recall the forms which they usually take and the manner in which they may be expected to die out. The intrusives are ordinarily known as batholiths, bosses, laccoliths, sills, and dikes. The extrusives are either lavas or tuffs. Frequently dikes radiate from a batholithic or laccolithic mass, become less and less abundant in passing away from the igneous mass, and finally disappear. Not infrequently the intrusives and extrusives are closely associated, intrusives being in one part of a region or district and equivalent extrusives in another part. But whether the rocks are intrusive or extrusive, if the quantity of igneous material be large and in various forms the igneous rocks usually do not die out at once, but gradually. Ordinarily the distance required for their disappearance is considerable, but in certain cases there are exceptions to this.

For the most part the ordinary masses of volcanic rocks do not profoundly affect the beds with which they are associated. On the other hand, large intrusive masses may metamorphose surrounding sediments for miles.

As a consequence of the gradual disappearance of eruptives under ordinary circumstances, the abundance of eruptives in one horizon and their absence in an adjacent horizon indicate that a structural break probably exists between the two, or that a fault has displaced the strata. The absence of phenomena which indicate faulting renders the first alternative probable. The sudden disappearance of eruptives is a particularly valuable criterion in separating adjacent series in cases in which parallel secondary structures have been induced in both. These secondary structures may have obliterated or nearly obliterated the original bedding, so that there may be none of the ordinary evidences of structural breaks; but if a set of dikes passes to a certain horizon and is suddenly cut off, this is very suggestive of an erosion interval between the two series. In cases of this kind the eruptives themselves are likely to have been extensively altered by the forces which produced the secondary structures in the sedimentary rocks; they may have been changed from their original condition to schists, and then may be shown to be dikes or intrusives by their structural behavior, by microscopical examination, or by chemical analysis.

When a series is cut by intrusives it sometimes happens that there is a difference in the erodibility of the dike and of the containing rock. In case the dike be more resistant, and the two were subjected to eroding agencies, it protrudes from the underlying formation, while in the opposite case there is a hollow. The latter is the condition of affairs described by Pumpelly at Hoosac Mountain, where an ancient dike cuts through the gneissoid granite. After a hollow of differential erosion was formed a sedimentary series was deposited. In approaching the dike the members of the sediments thicken somewhat and pass into the depression. The greater thickness of the lower beds at the hollow finally compensates for it, and the thickened beds gradually pass up into ordinary regularly stratiform beds. (Fig. 24.) In this case later orogenic movements produced consonant secondary structures both in the granite and in the overlying formations, and this relation of the dike to the two series was the first evidence found

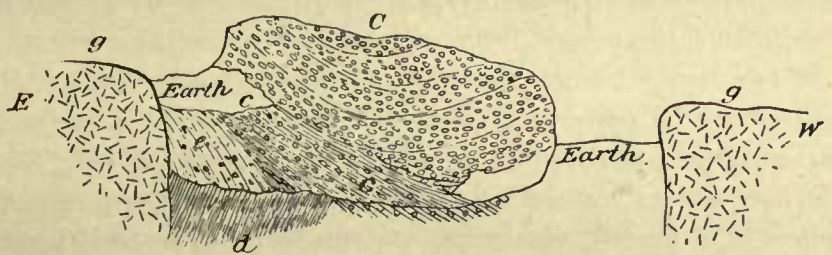

FIG. 24.—Conglomerate deposited in depression produced by erosion of basic dike through gneiss. After Pumpelly. *C*, conglomerate; *c*, lower layers of conglomerate rendered schistose by admixture of material from the altered dike; *d*, diabase of the dike rendered schistose by metamorphism; *e*, altered dike material; *g*, pre-Cambrian granitoid gneiss.

of a structural break between them. They had hitherto been considered as conformable, although a very close study had been made of them. Later other evidence confirmed this inferred unconformity.

In a different case the contacts between two unconformable series may not be found, but one series may be cut through and through by dikes and contain bosses of igneous material and interstratified intrusives or extrusives, with perhaps also volcanic fragmentals, while the adjacent set of formations may be wholly free from igneous rocks. Relations of this kind have force in proportion to the extensiveness of the phenomena. If one series is rich in igneous rocks for many miles, while another contiguous series is entirely free from them, and the irregular distribution of the two is such as not to be explained by faulting, the evidence of a structural break between the series is very strong.

In any of the above cases the time break between the two series must have been long enough for a full cycle of igneous activity.

In proportion as the igneous rocks are metamorphosed it is difficult to apply the above criteria. Where they are no longer distinguishable from the sedimentary rocks the criteria given for determining structural relations are not available.

RELATIONS OF ROCK FLOWAGE TO MOUNTAIN MAKING.

The principles of metamorphism worked out in the previous chapters have an important bearing upon theories of mountain making. Various authors have advocated expansion theories of mountain making. Probably the most notable of these is Reade. His explanation of the rise of mountains is that the volume of the thick deposits of sediments increases in consequence of the rise of the isogeotherms.[a] It is perfectly clear from the previous chapters that the alterations of the zone of anamorphism result in very important contraction. Not only is this true of the deep-seated zone, but in the zone of katamorphism the volume of one great class of sediments, the pelites, is certainly decreased both by consolidation and by dehydration. It may perhaps be conceded that the reactions of metamorphism, if all of geological time be taken into account, have somewhat expanded the volume of a very superficial belt of the earth. But in the deep-seated zone, where pressure is dominant, the reactions are taking place in a reverse sense, and as these have prevailed throughout geological time and to unknown depths, it can hardly be doubted that the contraction due to these deep-seated reactions is of vastly greater importance than the sum total of expansion due to superficial causes.

Perhaps it will be well to recall the facts bearing on the amount of contraction which takes place in consequence of the reactions of the zone of anamorphism.

It has been seen on page 364 that the average specific gravity of the minerals formed in the zone of anamorphism is about 18 per cent greater than that of those which develop in the zone of katamorphism; but for the rocks of the zone of anamorphism not all the minerals have passed to the products characteristic of that zone. Therefore, one can not premise that in the metamorphism of sedimentary rocks there is a diminution of volume as great as this. However, it is probable that the average of the chemical reactions of dehydration and silication and mechanical consolida-

[a] Reade, T. Mellard, Origin of mountain ranges: London, 1886, pp. 1–359.

tion give a decrease in volume of at least 10 to 15 per cent for the majority of the sediments. This is not believed to be an overestimate for the average of the pelites, psephites, and limestones, but the decrease in volume for the sandstones is probably not so great as this. It is therefore certain that the decrease in volume in consequence of reactions controlled by compression in the deep-seated zone is vastly greater than any expansion which can result from rise in temperature. And it is certain that from the top of the zone of anamorphism to the greatest depth to which observation extends the reactions of metamorphism tend to produce minerals of higher specific gravity. However, the entire zone of observation is very narrow as compared with the distance to the center of the earth. If the law observed continues to great depth, it would follow that deeper within the earth than observation extends minerals of specific gravity higher than any known are produced. There is every reason to believe that the density of the most densely crystallized minerals with which we are familiar is far from the maximum possible density. Hence, as pointed out on pages 364–365, deep within the earth, where the pressures are vastly greater than any with which we are familiar, it is certainly possible, and perhaps probable, that there exists a class of heavy minerals of complex molecules with which we are entirely unfamiliar.

But whether this speculation be well founded or not, there is every reason to believe that during geological time there has been steady condensation of the volume of the earth as a result of crystallization and recrystallization. For eras at least the earth has steadily lost heat, and magma has changed to crystallized rock, which has less volume. Probably also the pressures within the earth have increased in amount in consequence of decreasing rotation period, and increasing pressure promotes recrystallization, with the formation of heavy minerals. It seems to me highly probable that the decrease in volume due to the crystallization and recrystallization of rocks, with the production of minerals of high specific gravity, is probably one of the most potent of the processes which have resulted in diminished volume.[a] If this be so, it appears that the sum total of metamorphic processes is subordinate to the general law of gravity which steadily demands decreasing volume for the earth. Recognizing this law, I have elsewhere held that it can not be maintained that masses of the earth locally rise

[a] Van Hise, C. R., Estimates and causes of crustal shortening: Jour. Geol., vol. 6, 1898, pp. 59–60.

unless an equal or a larger mass elsewhere subsides—in short, that the center of gravity of the moved mass is nearer the center of the earth after the movement than before.[a] The expansion theory of mountain making is wholly controverted by the facts of metamorphism.

But mountain systems have been formed in some way, and during their building the material of the mountains has been uplifted even if material elsewhere has subsided. The uplifted areas are local. Indeed, it is because of localization that uplift can be recognized. As the geoid responds to the stresses within it, at least near the surface, the folding and faulting is largely concentrated in certain belts. It follows that the outer crust of the earth must have moved in some way over the interior. This fact of the localization of mountain masses and the resultant necessity that the crust should shear over the interior is one of the reasons which led the early geologists to adhere strongly to the existence of a liquid substratum. However, the physicists who have studied the earth with reference to tidal deformation insist that its interior is rigid; that if it were a liquid the attraction of the moon and sun would result in tides which would be shown in the crust of the earth.

It appears to me that the explanation of rock flowage offered on pages 748–759 shows how mountain masses may be segregated, the upper crust of the earth shearing over the deeper seated material for a long way without a liquid substratum. It has been explained that in the zone of anamorphism, under the deforming stresses of the earth, rocks flow by recrystallization. They are solid at the beginning of the process, throughout the process, and at the end of the process; and yet they have accommodated themselves to the form demanded by continuous solution and redeposition. It has further been somewhat fully explained (pp. 769–774) that the energy required for such deformation in the zone of flowage is not nearly so great as that required for deformation of an equal mass producing a similar form in the zone of fracture. In other words, the outer shell of the earth, the zone of fracture, is more rigid under slow deforming stresses than is a deeper seated zone which may be deformed by recrystallization. If this be so, we are able to see how the outer part of the lithosphere may shear over the zone below, as if it were a plastic

[a] Van Hise, C. R., Earth movements: Trans. Wisconsin Acad. Sci., Arts, and Letters, vol. 11, 1898, pp. 512–514.

stratum, and thus the necessary crustal shortening demanded for a large segment of the earth may be concentrated in a single mountain mass. This theory of the deformation of the zone of flowage by recrystallization meets the needs of the geologist who demands a substratum sufficiently plastic to be deformed under long-continued moderate stresses, and at the same time meets the demands of the physicist for a material so strong as to resist sudden stresses.

But it may be said that this hypothesis is a mere speculation, unsupported by any observation and with no possibility of support by observation. This is true if we consider the existing mountains, the last uplift of many and perhaps the majority of which occurred in Tertiary time. But before these mountains existed more ancient mountains existed, and denudation since early geological time has exposed many parts of the lithosphere over vast regions which were once thousands of meters below the surface. For instance, the Appalachian system of the United States, from Maine to Georgia, including the New England and Piedmont plateaus, has undergone deep erosion since Paleozoic time. Vast regions in Canada and in northern Europe have been subject to enormous, although perhaps interrupted, erosion since Cambrian time. In such regions observations show that there now exist at the surface extensive areas of rock which were deformed in the zone of rock flow.

Is there any evidence in such regions, from the character of the deformation and the structures which have been produced, that shearing has taken place in the same direction for considerable areas? Such evidence would support the view that equivalent shearing may have taken place in the present zone of rock flow, and thus have segregated the existing mountains. In another place I have shown that monoclinal cleavage may result from shearing motion in rocks parallel to the surface of the earth, there being no elongation or shortening in consequence of it.[a] This is illustrated by fig. 25, where a mass represented by *abcd* in the diagram at the left is sheared into the form shown in the diagram at the right, the lines *a–b*, *c–d* in both diagrams being supposed to be parallel to the surface of the earth. The position of the cleavage is indicated by the longer diameters of the flattened ellipsoids. If this sort of deformation should take place over an extensive area in the zone of flow, it might

[a] Van Hise, C. R., Estimates and causes of crustal shortening: Jour. Geol., vol. 6, 1898, pp. 29–31.

transport the superjacent material of the zone of fracture with it, and thus carry forward the upper crust of the earth toward the mountain mass and allow the segregation of all of the superficial deformation in one belt.

It is to be noted that in the theoretical case illustrated by the diagram there is no crustal shortening of the belt in the zone of fracture or of the material of the zone of flowage. The material has merely changed its position with reference to the surface of the earth

From the foregoing it is not to be supposed that monoclinal cleavage has generally been produced without any plications or crustal shortenings. Indeed, in areas in which monoclinal cleavages are prevalent there may be numerous folds, as, for instance, in the New England region and in the Blue Ridge area. No doubt in cases where the deformation is consider-

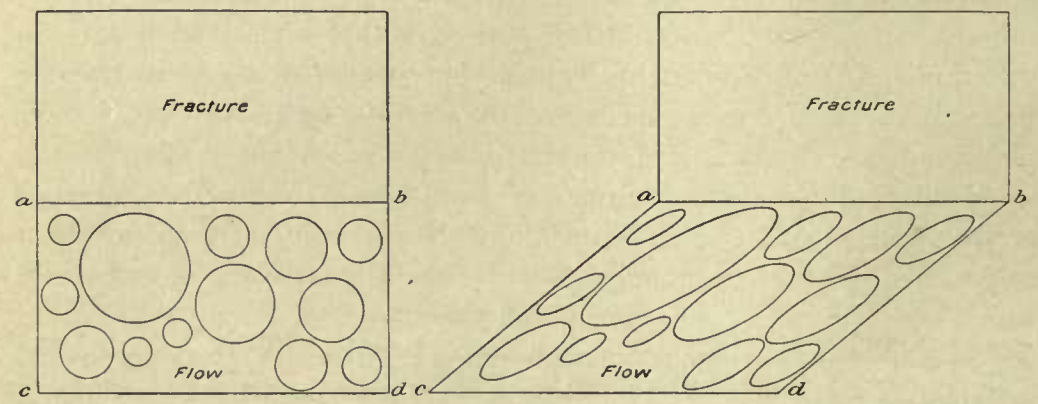

FIG. 25.—Diagrams illustrating the manner in which deformation in the zone of flowage may concentrate crustal shortening in the zone of fracture.

able there are all gradations, from very little or no crustal deformation of the superjacent rocks to that of the complex kind which is characteristic of the local zones of intense deformation. And even if the suggestion be true in general, it is believed that in any instance there is likely to be more or less of monoclinal folding in connection with the monoclinal cleavage, and consequently more or less of crustal shortening. However, it is thought that the hypothesis affords a possible explanation of the concentration of the greater part of the crustal shortening in local zones.

The question now arises whether, in the regions of the earth in which the past zone of flowage is now at the surface, monoclinal cleavage exists. That such cleavage does exist for some extensive regions is well known. For instance, the crystalline area of the Appalachian system from Maine to Georgia shows a dominant easterly dipping cleavage.

Where mountain systems exist with monoclinal folds or with thrust faults the segregations may be explained by shearing motion in the zone of flow over an extensive adjacent area to the east of the mountain mass in case the monoclinal folds have eastward-dipping axial planes, and to the west of the mountain mass in case the monoclinal folds have westward-dipping axial planes. (Fig. 25.) Where the folds of a mountain system are symmetrical it would be necessary to suppose that the shearing motion toward the mountain mass occurred on both sides of it.

To illustrate, we may consider one of the large, simple anticlinoria, such as those of the Park Ranges. We may suppose that such an anticlinorium was raised mainly in consequence of deep-seated flow toward the mountain mass from either side. In this case the cleavage on either side of the mountain would dip away from it. It is well known that the present Park Ranges are comparatively recent uplifts along axes of old uplifts. Some of the recent uplifts are partly or wholly covered by Paleozoic and later strata. In the cases of these simple anticlinoria of the West the cleavages of the old rocks on both sides of the anticlinal masses dip away from the cores. Indeed, because of this fact, in the days when cleavage was not discriminated from primary structures the cleavage was supposed to be bedding, and upon the basis of this structure the mountains were described as anticlinal. The present mountains we may properly describe as anticlinal with reference to the Paleozoic and post-Paleozoic rocks which rest upon their flanks. But since we know that mountains rise again and again along the old belts, the cleavage, dipping away from the cores of these mountain masses, is very suggestive that when the ancient higher mountains were developed the material was segregated in consequence of deep-seated flow by recrystallization toward the mountain masses, there being produced at this time the divergent cleavage existing in the pre-Cambrian rocks which are now at the surface, but which were well below the surface when the cleavage was produced.

The cores now exposed were covered by rocks deformed in the zone of fracture and showed the deformation of joints, joint folds, faults, etc., characteristic of the superficial zone. The deep-seated flowage extended for an unknown distance on either side of the mountains, and thus brought to the place of uplift the necessary material. The covering rocks belonging to the zone of fracture on either side of the mountain range may be

conceived as riding quietly forward toward the uplift without marked deformation.

Applying this theory, we may imagine that the Kaibab Plateau, for instance, on either side flanked by a monocline, represents an uplift which is produced by deep-seated shear from either side toward the plateau, producing simultaneously a cleavage or a tendency toward a cleavage in the zone of flowage. Such cleavage would dip away from the plateau on each side of it. The joint and fault deformations exhibited by the monoclines in the zone of fracture represent the equivalent necessary superficial deformation.

Where the folds of a mountain range are symmetrical and upright it would be necessary to suppose that there was an equal amount of deep-seated shearing on each side toward the mountain mass. Where the axial planes of the structures of the mountain masses tend to dip in one direction more than in another it is to be supposed that the preponderant movement came from the direction in which the axial planes dip.

Possibly the suggestion of recrystallization shearing in the zone of rock flowage also has a bearing upon the importance of the tidal forces in producing deformation. It has been noted that in America the eastward-dipping monoclinal cleavage tends to preponderate over the westward-dipping cleavage. The same is true for monoclinal folding. This is especially marked for the eastern United States and Canada. How far it is true over the extensive areas of pre-Cambrian rocks of central Canada is uncertain. Whether in other continents there is a preponderance of eastward-dipping cleavage over westward, and of monoclinal folding with eastward-dipping axial planes over the reverse, I do not know and have been unable to ascertain; but it is interesting to note that if these easterly structures are preponderant they are in the right direction to be genetically connected with tidal friction. The earth in its rotation upon its axis from west to east produces a westward-moving tide. The same force which acts upon the water acts upon the rocks below, or, in other words, tends to slip the outer shell of the earth over the deeper shells. Such slipping, if it takes place through the processes of recrystallization in the zone of rock flowage, would produce an eastward-dipping monoclinal cleavage and monoclinal folds with eastward-dipping axial planes.

If Darwin and Peirce are correct in thinking that the moon was once very close to the earth, and that at this early time the earth had a much briefer rotation period than at present, the tidal force tending to produce such monoclinal structures in the zone of flow would be vastly greater than at present. It is worthy of note that the preponderant easterly structures which have been noted are among the Paleozoic and pre-Paleozoic rocks which in post-Paleozoic time have been brought to the surface in consequence of denudation. If more extended and closer geological studies of cleavage and monoclinal folding lead to the conclusion that easterly structures do preponderate over westerly structures for the earth as a whole, it may be plausibly argued that these phenomena in the old rocks are geological evidence of the correctness of Darwin's general theory in reference to the earth-moon couple, and that the tidal forces in the past were vastly greater than those which now exist.[a]

I am aware that the foregoing pages upon the relations of rock flowage to mountain making are speculative, but the speculations accord, so far as I know, with the facts of the field. They are here published in the hope that they may lead to more accurate observations of the relations of primary and secondary structures to each other, and of the positions of secondary structures in various mountain regions. Concerning these points I have found the published literature upon the metamorphic rocks woefully lacking.

[a] Darwin, G. H., On the precession of a viscous spheroid and on the remote history of the earth: Philos. Trans. Royal Soc., vol. 170, pt. 2, 1879, pp. 530–538.

CHAPTER XI.

RELATIONS OF METAMORPHISM TO THE DISTRIBUTION OF THE CHEMICAL ELEMENTS.

In consequence of metamorphism the chemical elements are redistributed on the face of the earth. This redistribution concerns many large questions of geological theory. At the present time our knowledge of metamorphism is not sufficiently advanced to treat the redistribution of the elements except in a very imperfect manner. In the following pages an attempt is made to consider the original source of each of the important chemical elements composing the outer part of the earth, and the effect which the metamorphic processes have had on its redistribution and on the character of the secondary rocks. So far as practicable redistribution is dealt with in a quantitative way, but a quantitative treatment is necessarily subject to the very imperfect hypotheses upon which it is based. Indeed, for the most part the quantitative estimates are the roughest sort of approximations, made more with a view of stating the various problems which in the future will undoubtedly be satisfactorily treated quantitatively rather than with the belief that the calculations given even approach accuracy. They are all purely provisional, and it is hoped that they will be considered from this point of view. Indeed, this chapter is no more than an attempt to blaze a trail in the wilderness. It will require the work of many men for many years to conquer the wilderness.

COMPOSITION OF THE LITHOSPHERE.

The term lithosphere as used in this chapter is rigidly restricted to that part of the solid crust of the earth of which we have observational knowledge, and which, following Clarke, is assumed to extend to a depth of only 10 miles (16.1 kilometers) below the level of the sea. According to R. S. Woodward, the volume of the part of the earth that is above the sea and that extends to a depth of 10 miles (16.1 kilometers) below the level of the

sea is 1,935,000,000 cubic miles (8,075,000,000 cubic kilometers). Of this amount 302,000,000 cubic miles (1,260,000,000 cubic kilometers) are ocean and 1,633,000,000 (6,815,000,000 cubic kilometers) are solid matter. The mass of the atmosphere is equivalent to that of 1,268,000 cubic miles (5,292,000 cubic kilometers) of water, the unit of density. "To sea water we may assign a density of 1.03, which is a trifle too high, and to the solid rocks a specific gravity not lower in average than 2.5, nor much higher than 2.7. With these values we can get the following expression for the percentage composition of the known matter of the globe:

Relative masses of air, sea, and earth's crust.

Per cent.	Density of crust 2.5.	Density of crust 2.7.
Atmosphere	0.03	0.03
Ocean	7.08	6.58
Solid crust	92.89	93.39
	100.00	100.00

In short, we may regard the earth's crust, to a depth of 10 miles [16.1 kilometers], as composed essentially of 93 per cent solid and 7 per cent liquid matter, treating the atmosphere as a small correction."[a]

A large number of elements have been discovered on the earth, but of these, according to Clarke, only 21 each constitute as much as 0.01 per cent of the outer part of the lithosphere, and need be considered in this chapter. Those elements which compose more than 1 per cent may be regarded as abundant and those which form less than 1 per cent as subordinate. Of the former class there are only eight, viz: Oxygen, silicon, aluminum, iron, calcium, magnesium, sodium, and potassium. Between the least plentiful of the abundant class and the most plentiful of the subordinate class there is a very considerable break, for potassium, the least plentiful of the abundant elements, makes up about 2.3 per cent of the lithosphere, while titanium, the most abundant of the subordinate elements, composes only about 0.4 per cent of the lithosphere.

In the chemical laboratory of the United States Geological Survey a very large number of analyses of rocks have been made. Clarke has

[a] Clarke, F. W., The relative abundance of the chemical elements: Bull. U. S. Geol. Survey, No. 78, 1891, pp. 34–35.

compiled these and other analyses, with the purpose of obtaining an approximate idea of the composition of the lithosphere. In his computations Clarke has considered only the "igneous and crystalline rocks." As these terms are used there are excluded from consideration the unmetamorphosed sediments and the metamorphosed sediments so far as they are recognized as sediments. In the following table are found the analyses of various groups of 880 igneous and crystalline rocks, and the mean of the whole:

Analyses of igneous and crystalline rocks.[a]

	A.	B.	C.	D.	E.	F.	G.	H.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
SiO_2	61.89	61.89	60.49	60.66	60.50	59.80	56.75	58.59
Al_2O_3	15.71	15.73	16.08	15.46	14.30	14.65	14.90	15.04
Fe_2O_3	1.81	3.18	2.47	2.74	3.35	4.99	4.58	3.94
FeO	3.65	2.40	2.86	2.27	4.31	2.92	3.71	3.48
CaO	4.51	4.58	6.15	4.71	3.52	5.19	5.79	5.29
MgO	2.40	3.08	4.31	3.35	5.00	3.45	5.22	4.49
K_2O	3.54	2.70	1.80	3.97	2.52	3.06	2.90	2.90
Na_2O	3.28	3.70	3.31	3.54	2.49	2.98	3.24	3.20
H_2O	1.69	1.59	1.12	.97	2.53	2.09	2.12	1.96
Total	98.48	98.85	98.59	97.67	98.52	99.13	99.21	98.89
ELEMENTARY SUBSTANCES.								
Si	28.88	28.88	28.23	28.31	28.23	27.91	26.50	27.34
Al	8.31	8.32	8.51	8.18	7.57	7.75	7.89	7.96
Fe	4.11	4.09	3.96	3.68	5.71	5.77	6.09	5.47
Ca	3.22	3.27	4.39	3.37	2.51	3.71	4.13	3.78
Mg	1.44	1.85	2.58	2.01	3.00	2.07	3.13	2.69
K	2.94	2.24	1.49	3.29	2.09	2.54	2.41	2.41
Na	2.43	2.74	2.46	2.63	1.85	2.21	2.56	2.37
H	.19	.18	.12	.11	.28	.23	.24	.22
O	46.96	47.28	46.85	46.09	47.28	46.94	46.26	46.65
Total	98.48	98.85	98.59	97.67	98.52	99.13	99.21	98.89

[a] Clarke, F. W., The relative abundance of the chemical elements: Bull. U. S. Geol. Survey No. 78, 1891, pp. 36–37.

A. The mean of 82 analyses of volcanic rocks from the Western Territories of the United States, published in Clarence King's Survey of the Fortieth Parallel.

B. 64 analyses of rocks from the Yellowstone Park, taken from the laboratory records of the United States Geological Survey.

C. 54 analyses of volcanic rocks collected in northern California; also from the Survey records.

D. 39 analyses of eruptive rocks from various localities in the Western United States, taken from the Survey records.

E. 80 crystalline and Archean rocks from all parts of the United States. Of these analyses 50 were taken from the Survey records, 23 from the Fortieth Parallel Report, and 7 from the report of the New Hampshire Survey, vol. 3.

F. 75 analyses of European volcanic and crystalline rocks, taken at random from five recent volumes of the Neues Jahrbuch.

G. 486 miscellaneous plutonic rocks, analyzed between 1879 and 1883, and collected by Roth in his "Beiträge zur Petrographie der plutonischen Gesteine."

H. The mean of the foregoing 880 analyses.

Clarke remarks that the columns A to F are remarkably accordant, and further says: "The thesis that the crust of the earth is fairly homogeneous in composition is thus sustained by positive evidence. The variations in the foregoing table are as small as could reasonably be expected."[a]

Clarke, in 1891, made an estimate of the composition of the lithosphere, of the ocean, and of the mean of the lithosphere, ocean, and air, but many of the analyses upon which this first estimate of the composition of the lithosphere was based were "incomplete regarded from a modern point of view." In 1900 Clarke therefore reestimated the composition of the lithosphere, basing the estimate upon 830 complete analyses of rocks and 400 partial analyses. Also, he computed the ten most important elements as oxides both for his first and second estimates of the lithosphere. His results are given in the following tables.

[a] Clarke, cit., p. 37.

Symbols, atomic weights,[a] *and proportions of the twenty-three most abundant elements in the outer 10 miles of the earth.*[b]

Name.	Symbol.	Atomic weight.	Estimate in 1891.			Estimate in 1900.
			Solid crust, 93 per cent.	Ocean, 7 per cent.	Mean, including air.	Solid crust.
Oxygen	O	16.00	47.29	85.79	49.98	47.02
Silicon	Si	28.4	27.21	.....	25.30	28.06
Aluminum	Al	27.1	7.81	.....	7.26	8.16
Iron	Fe	56.00	5.46	.....	5.08	4.64
Calcium	Ca	40.00	3.77	.05	3.51	3.50
Magnesium	Mg	24.36	2.68	.14	2.50	2.62
Sodium	Na	23.05	2.36	1.14	2.28	2.63
Potassium	K	39.15	2.40	.04	2.23	2.32
Titanium	Ti	48.1	.33	.....	.30	.41
Hydrogen	H	1.01	.21	10.67	.94	.17
Carbon	C	12.00	.22	.002	.21	.12
Phosphorus	P	31.00	.10	.....	.09	.09
Manganese	Mn	55.00	.08	.....	.07	.07
Sulphur	S	32.06	.03+	.09	.04+	.07
Barium	Ba	137.4	.03	.....	.03	.05
Strontium	Sr	87.6	.....	.....	.....	.02
Chromium	Cr	52.1	.01	.....	.01	.01
Nickel	Ni	58.7	.....	.....	.....	.01
Lithium	Li	7.03	.....	.....	.....	.01
Chlorine	Cl	35.45	.01	2.07	[c].15	.01
Fluorine	F	19.00	.....	.....	.....	.01
Bromine	Br	79.96	.....	.008	.....	.....
Nitrogen	N	14.04	.....	.....	.02	.....
Total	.....	.....	100.00	100.00	100.00	100.00

[a] In Chapter V, page 193, the list of atomic weights is given on the basis of hydrogen as 1. The table of rock-making minerals is also constructed on this basis. However, so far as the results of increase and decrease in volume of the minerals are concerned, it makes no difference whether hydrogen be taken as 1 and oxygen as 15.88, or whether oxygen be taken as 16 and hydrogen as 1.01. As the more common practice of the chemists is to use oxygen as 16, the table of atomic weights here given is on that basis. See Wiechmann, F. G., Atomic weights: Science, vol. 9, 1899, p. 23.

[b] Clarke, F. W., Report of work done in the Division of Chemistry and Physics, 1889–90: Bull. U. S. Geol. Survey No. 78, 1891, p. 36. Clarke, F. W., Analyses of rocks, laboratory of the U. S. Geological Survey, 1880–1899: Bull. U. S. Geol. Survey No. 168, 1900, p. 15.

[c] With bromine.

Amounts of the eleven most important oxides of the lithosphere, as estimated in 1891 and 1900.[a]

	Old mean.	New mean.		Old mean.	New mean.
SiO_2	58.59	59.71	K_2O	2.90	2.80
Al_2O_3	15.04	15.41	H_2O	*1.96	1.52
Fe_2O_3	3.94	2.63	TiO_2	.55	.60
FeO	3.48	3.52	P_2O_5	.22	.22
MgO	4.49	4.36	Total	99.66	99.22
CaO	5.29	4.90			
Na_2O	3.20	3.55			

*Including hygroscopic water; probably 0.40 per cent.

Clarke further made a rough approximation of the proportion of the more important minerals in 500 igneous rocks, as follows:[b]

Important minerals in 500 igneous rocks.

	Per cent.
Quartz	12.0
Feldspars	60.0
Pyroxenes and amphiboles	18.0
Micas	4.0
Total	94.0

The foregoing estimates are wholly based upon the analyses of "eruptive and crystalline" rocks, and represent, according to Clarke's point of view, the average composition of the "primitive crust of the earth." In these analyses all of the unmetamorphosed and metamorphosed sediments, so far as they are recognized as such, are excluded. As we shall see later, the unmetamorphosed sediments probably compose as much as one-thirtieth and the unmetamorphosed and metamorphosed sediments may together comprise as much as one-fifteenth of the lithosphere. The average composition of the sediments is of the utmost importance in reference to a redistribution of the elements. Clarke has had made six composite analyses of groups of

[a] Clarke, F. W., Analyses of rocks, laboratory of the U. S. Geol. Survey, 1880–1899: Bull. U. S. Geol. Survey No. 168, 1900, p. 14.

[b] Clarke, cit., p. 16.

sedimentary rocks, in which 1,545 rocks were taken into consideration. The table below gives his results.

Composite analyses of sedimentary rocks.[a]

	A.	B.	C.	D.	E.	F.	G.	H.	I.
SiO_2	55.43	60.15	58.38	78.66	84.86	81.76	5.19	14.09	9.64
Al_2O_3	13.84	16.45	15.47	4.78	5.96	5.37	.81	1.75	1.28
Fe_2O_3	4.00	4.04	4.03	1.08	1.39	1.24	.54	.77	.66
FeO	1.74	2.90	2.46	.30	.84	.57	Undet.	Undet.	Undet.
MgO	2.67	2.32	2.45	1.17	.52	.85	7.90	4.49	6.20
CaO	5.96	1.41	3.12	5.52	1.05	3.29	42.61	40.60	41.60
Na_2O	1.80	1.01	1.31	.45	.76	.61	.05	.62	.34
K_2O	2.67	3.60	3.25	1.32	1.16	1.24	.33	.58	.46
H_2O at 110°	2.11	.89	1.34	.31	.27	.29	.21	.30	.26
H_2O above 110°	3.45	3.82	3.68	[b]1.33	[b]1.47	1.40	[b].56	[b].88	.72
TiO_2	.46	.76	.65	.25	.41	.33	.06	.08	.07
CO_2	4.62	1.46	2.64	5.04	1.01	3.03	41.58	35.58	38.58
P_2O_5	.20	.15	.17	.08	.06	.07	.04	.42	.23
SO_3	.78	.58	.65	.07	.09	.08	.05	.07	.06
Cl	------	------	------	Trace.	Trace.	Trace.	.02	.01	.01
S	------	------	------	------	------	------	.09	.07	.08
MnO	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.	.05	.03	.04
BaO	.06	.04	.05	.05	.01	.03	None.	None.	None.
SrO	None.	None.	None.	Trace.	None.	Trace.	None.	None.	None.
Li_2O	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.	Trace.
Carbon[c]	.69	.88	.81	------	------	------	------	------	------
	100.48	100.46	100.46	100.41	99.86	100.16	100.09	100.34	100.23

A. Composite analysis of 27 Mesozoic and Cenozoic shales. Each individual shale was taken in amount roughly proportional to the mass of the formation which it represented.

B. Composite analysis of 51 Paleozoic shales, weighted as in the former case.

C. General average of A and B, giving them respectively weights as 3 to 5. This average represents 78 rocks.

D. Composite analysis of 253 sandstones, about 1 gram of each being taken in preparing the average sample.

E. Composite analysis of 371 sandstones used for building purposes, equal weights taken.

F. Average of D and E, total of 624 sandstones. The sandstones selected at random and those used for building purposes are given equal weights.

G. Composite analysis of 345 limestones, equal weights being taken.

H. Composite analysis of 498 limestones used for building purposes, equal weights taken.

I. Average of G and H, total of 843 limestones. The limestones selected at random and those used for building purposes are given equal weights.

[a] Clarke, F. W., Analyses of rocks, laboratory of the U. S. Geol. Survey, 1880–1899: Bull. U. S. Geol. Survey No. 168, 1900, pp. 16–17.

[b] Includes organic matter.

[c] Of organic origin.

Various estimates, which are little more than guesses, have been made of the thickness of the sedimentary rocks upon the earth. Dana in 1875 stated that the mean thickness of the sediments for the continental areas will not exceed 5 miles (8.05 kilometers).[a] T. Mellard Reade states that an estimate of 10 miles (16.1 kilometers) is a moderate one for the thickness of the sedimentary crust of the earth throughout.[b] Later he greatly reduces this estimate, saying: "I think we may with safety provisionally assume that the actual average thickness of the sedimentary crust of the globe is not less than 1 mile (1.61 kilometers)."[c] This average is for the globe as a whole, and not for the continental areas, and therefore is not greatly below Dana's estimate of 8 kilometers for the continents alone. It appears to me that even Reade's revised estimate is much too great. At only a very few localities can it be shown that the thickness of the sediments approximates 8 kilometers. For the great plains and plateau areas where there are deep borings or deep gorges, as, for instance, in the Grand Canyon, the sediments frequently do not exceed 1 kilometer, and in general are less than 2 kilometers. For great areas of the continents, such as extensive Archean areas of Canada, there are no known sediments. For the greater part of the ocean, aside from the continental shelves, all the evidence available points toward very slow deposition, and over such areas, composing about two-thirds of the surface of the globe, the sediments are probably of inconsiderable thickness.

The area of the globe is approximately 500,000,000 square kilometers, of which somewhat more than one-fourth belongs to the continents and continental shelves. If it were supposed that the sediments which have not been within the zone of anamorphism, but have always remained in the zone of katamorphism, are upon an average 2 kilometers thick for the continents, this would give 250,000,000 cubic kilometers of sediments. This estimate is, of course, little more than a guess, made in order that a number of problems in the distribution of the elements may be quantitatively stated. In comparing this estimate with that of Dana or Reade it should also be noted that mine includes only sediments of the zone of katamorphism—not those which have been metamorphosed in the zone of anamorphism—while Reade's estimate includes both.

[a] Dana, James D., Manual of Geology, second edition, 1875, p. 657.
[b] Reade, T. Mellard, Chemical denudation in relation to geological time, p. 29.
[c] Loc. cit., p. 52.

On the supposition that the sediments of the zone of katamorphism are 2 kilometers thick, they compose about 3.668 per cent of the volume of the lithosphere to a depth of 16.1 kilometers (10 miles) below the level of the sea (6,815,000,000 cubic kilometers). With a specific gravity of 2.7 the weight of the sediments would be 675,000,000,000,000,000 metric tons.

In suggesting the above figures the aim has been to underestimate rather than to overestimate the total amount of the sediments. It is thought better to have the calculated amount of elements required for certain changes smaller than the real amounts rather than larger. For instance, it will be explained on the following pages that the change of ferrous to ferric oxide in the sediments has required a vast amount of oxygen—indeed, an amount so great as to be a large percentage of the total oxygen now present in the atmosphere. If an overestimate of the total mass of sediments were made, this would lead to an overestimate of the amount of oxygen required for this change. But the purpose is to make the estimate of the amount of oxygen and of the other elements required for this and for other changes less than the real amounts rather than more.

In making the first rough approximation of the weight of the sediments, they will all be supposed to have a specific gravity of 2.7. While the specific gravity of sediments varies, and doubtless upon the average is somewhat less than 2.7 (the average of the igneous and crystalline rocks), the error in placing it at 2.7 is small compared with the errors in the estimates of the amount of sediments and their relative proportion. Therefore, for convenience in the present provisional calculations, a uniform specific gravity for the rocks of the lithosphere is assumed. If the sediments of the zone of katamorphism were supposed to be 0.65 shales and other rocks largely composed of silicates (pelites and psephites), 0.30 sandstones, and 0.05 limestones, this would give 162,500,000 cubic kilometers of shales, weighing 438,750,000,000,000,000 metric tons, 75,000,000 cubic kilometers of sandstones, weighing 202,500,000,000,000,000 metric tons, and 12,500,000 cubic kilometers of limestones, weighing 33,750,000,000,000,000 metric tons. In the following pages the term shale will be understood to include all the clastic sedimentary rocks rich in silicates.

So far as I know there has been no attempt to estimate accurately the relative quantities of shales, sandstones, and limestones. The above partition of the sediments is the roughest sort of a guess. The only computation

which I am aware of on the subject is in reference to limestone. T. Mellard Reade, by comparing the amount of calcium carbonate and calcium sulphate in solution in rivers with the sediments mechanically carried by rivers, concluded that one-eighth to one-ninth of the transported material is composed of the carbonate and sulphate of calcium. Using his estimate of a thickness of 1 mile for the sedimentary rocks, and supposing that the mass of limestone is one-tenth of the whole mass of the rock, he says: "This gives us the equivalent of a zone of limestone rock 528 feet (160.9 meters) thick, enveloping the globe, as a very rude approximation to the absolute quantity of carbonate and sulphate of lime in the sedimentary crust of the earth."[a] Of the two compounds calcium carbonate so dominates over calcium sulphate that the latter will be neglected and the whole will be considered as calcium carbonate.

If the amount of calcium carbonate carried by the streams at present is not an accurate measure of the average carried by streams through geological time, the error is likely to be an overestimate rather than an underestimate, since early in geological times, before the calcareous sediments had accumulated, it can not be supposed that the streams carried as much calcium carbonate as at present. Further, the method of computation used by Reade for estimating the volume of the limestones is rather unsatisfactory, since it is certain that a considerable portion of the calcium carbonate passes into shales and sandstones, as is shown by the analyses (p. 938).

The shales contain 2.64 per cent of carbon dioxide and the sandstones 3.03 per cent. If most of this carbon dioxide is united with calcium oxide, as is probable, this would give about 5 per cent, or one-twentieth, of calcium carbonate in the shales and sandstones. Therefore, if the shales and sandstones were supposed to be nineteen times as abundant as the limestones, these rocks would require one-half of the calcium carbonate, and the proportion of limestone instead of being one-tenth, as estimated by Reade, would be one-twentieth of the total mass of the sediments. This ratio of 19:1 between the sandstones and shales together and the limestones is accordant with the relative amounts of the rocks as calculated upon the basis of depletion of calcium oxide in the sandstones and shales as compared with the original rocks (see pp. 990–991). It thus appears that the estimate of one-twentieth, or 0.05, of the mass of sediments for limestone, is probably as near the truth as can be made from data at the present time.

[a] Reade, T. Mellard, Chemical denudation in relation to geological time, p. 53.

As a result of the work of the *Challenger* expedition, the ocean is estimated to have a volume of 1,283,840,000 cubic kilometers.[a] This estimate, equivalent to 307,000,000 cubic miles, is somewhat in excess of Woodward's estimate of 302,000,000 cubic miles, given on page 933. The weight of 1,283,840,000 cubic kilometers of the ocean, with a specific gravity of 1.03 (see p. 933), is 1,322,355,000,000,000,000 metric tons. Of this 85.79 per cent, or 1,134,448,354,500,000,000 metric tons, is oxygen, and 10.67 per cent, or 141,095,278,500,000,000 metric tons, is hydrogen. Taking the maximum salinity of sea water as given by Dittmar,[b] 37.37 grams of salts per kilogram of water, sea water is 96.263 per cent water and 3.737 per cent salts. The 3.737 per cent salts is made up of the following compounds:

Composition of salts in sea water.[c]

	Per cent.
Chlorine	55.292
Bromine	.1884
Sulphuric oxide (SO_3)	6.410
Carbon dioxide (CO_2)	.152
Lime (CaO)	1.676
Magnesia (MgO)	6.209
Potash (K_2O)	1.332
Soda (Na_2O)	41.234
Oxygen equivalent of halogen	—12.493
Total	100.000

[a] Dittmar, William, Composition of ocean-water salts: Narrative of the cruise of H. M. S. *Challenger*, vol. 1, pt. 2, 1885, pp. 951, 980.

[b] Dittmar, William, Report of the scientific results of the exploring voyage of H. M. S. *Challenger*, 1873–1876: Vol. I, Physics and Chemistry, London, 1884, p. 201.

[c] Dittmar, Narrative of the cruise, etc., p. 954.

Combining acids and bases, we have the following average composition of sea salt:[a]

Percentages of salts in sea water.

	Per cent.
Chloride of sodium	77.758
Chloride of magnesium	10.878
Sulphate of magnesium	4.737
Sulphate of lime	3.600
Sulphate of potash	2.465
Bromide of magnesium	.217
Carbonate of lime	.345
Total	100.000

From the above table the percentages of the different elements in the ocean salts are calculated as follows:

Percentages of elements in sea salt.

	Per cent.		Per cent.
Cl	55.217	K	1.107
Na	30.637	Br	.188
O	5.283	C	.041
Mg	3.769	Total	100.000
S	2.562		
Ca	1.196		

The total amount of these compounds as calculated by Dittmar is 46,283,000,000,000,000 tons, or 46,283 ($10^{12} \times 1{,}000$) kilograms. The amounts of the different compounds are given in the table below.[b]

Total amounts of salts in the ocean.

[Unit=10^{12} metric tons.]

Chloride of sodium ($NaCl$)	35,990
Chloride of magnesium ($MgCl_2$)	5,034
Sulphate of magnesium ($MgSO_4$)	2,192
Sulphate of calcium ($CaSO_4$)	1,666
Sulphate of potash (K_2SO_4)	1,141
Bromide of magnesium ($MgBr_2$)	100
Carbonate of calcium ($CaCO_3$)	160
	46,283

[a] Dittmar, Narrative of the cruise, cit., p. 954.

[b] Dittmar, cit., p. 980.

Taking the above estimates, the amounts of the different elements of the ocean salts are given in the following table:

[Unit=10^{12} metric tons.]

Cl	25,557	K	512
Na	14,180	Br	87
O	2,445	C	19
Mg	1,743		
S	1,187	Total	46,283
Ca	553		

Clarke, using the above results of Dittmar, computes the elemental composition of the ocean, as already given (p. 936); but for convenience his results are here repeated:[a]

Composition of ocean.

O	85.79	K	0.04
H	10.67	S	.09
Cl	2.07	Br	.008
Na	1.14	C	.002
Mg	.14		
Ca	.05	Total	100.000

Excluding the subordinate constituents, air has the following composition:

Composition of air.

	By volume.	By weight.
	Per cent.	*Per cent.*
Nitrogen	79.08	76.88
Oxygen	20.92	23.12

The amount of carbon dioxide in the air is 0.03 per cent by volume and 0.045 per cent by weight.[b] There are also in the air minute proportions of water vapor, ammonia (NH_3), argon, etc.

According to Woodward (see p. 933) the mass of the atmosphere is equivalent to that of 5,292,000 cubic kilometers (1,268,000 cubic miles) of water of unit density. This is equal to a weight of 5,292,000,000,000,000 metric tons. Disregarding the subordinate elements, the weight of the nitrogen would be 4,068,489,600,000,000 metric tons, and of the oxygen 1,223,510,400,000,000 metric tons.

[a] Clarke, F. W., Relative abundance of the chemical elements: Bull. U. S. Geol. Survey No. 78, 1891, p. 35.

[b] Mendeléeff, D., The principles of chemistry, translated by George Kamensky: Longmans, Green, & Co., London, 6th ed., vol. 1, 1897, pp. 235, 236, and 238.

The above data give the approximate composition of the lithosphere as now constituted; but not of the earth as a whole. As pointed out by Farrington,[a] we can probably get a rough approximation to the composition of the earth by considering the nature of meteoric falls, as they are supposed to furnish the best basis for estimating the composition of the material out of which the world has segregated. Meteoric falls rather than meteoric finds are chosen because "the iron meteorites are much more likely to be known and preserved than the stony."[b] The average specific gravity of meteoric falls, as determined by Farrington, is 3.69.[c] No attempt has been made to estimate quantitatively the proportions of the elements which compose such meteorites, taking into account both their masses and compositions. However, Farrington[d] recently considered the mineral and chemical compositions of various classes of meteorites, including both falls and finds, and in some cases gave the relative proportions of a few of the elements in these, and the percentages of a few of the minerals in some of the meteorites considered. From his article the following table is made:

Constituents of meteorites.

Name.	Composition.	Relative proportions.	Percentage of total of definite meteorites.
	ESSENTIAL.	*Per cent.*	
Nickel-iron	Alloy of Ni and Fe	Ni 6–20 (Co .5–2) (Cu .006–.02)	
Chrysolite	$(MgFe)_2SiO_4$	Fe 10–30 Ni almost lacking.	
Orthorhombic pyroxenes	All gradations between: $MgSiO_3$ (enstatite) $(MgFe)SiO_3$ (bronzite) $(FeMg)SiO_3$ (hypersthene)		
Monoclinic pyroxenes:			
Augite	$Ca(MgFe)(SiO_3)_2$ with $(MgFe)(AlFe)_2SiO_6$		
Diopside	$CaMg(SiO_3)_2$ $Ca(MgFe)(SiO_3)_2$		
Plagioclase:			
Anorthite	$CaAl_2Si_2O_8$		35 (2 meteorites).
Albite	$NaAlSi_3O_8$		
Oligoclase	Ab_6An_1 to Ab_3An_1		
Labradorite	AbAn (1:1 or 1:3)		
Maskelynite	About same as labradorite		22.5 (1 meteorite).

[a] Farrington, O. C., The average specific gravity of meteorites: Jour. Geol., vol. 5, 1897, pp. 127–128.
[b] Farrington, The constituents of meteorites: Jour. Geol., vol. 9, 1901, p. 394.
[c] Farrington, The average specific gravity of meteorites: Jour. Geol., vol. 5, 1897, p. 130.
[d] Farrington, The constituents of meteorites: Jour. Geol., vol. 9, 1901, pp. 393–408, 522–532.

Constituents of meteorites—Continued.

Name.	Composition.	Relative proportions.		Percentage of total of definite meteorites.
	ACCESSORY.			
Included gases:		Iron.	Stone.	
H		63.09	17.55	
CO		20.70	4.15	
CO_2		8.12	71.66	
N		7.52	2.20	
CH_4		0.57	4.17	
		100.00	99.73	
Iron sulphide:				
Troilite	FeS.			
Pyrrhotite (?)	FeS.			
Schreibersite	$(FeNiCo)_3P$	Most widely distributed constituent of *iron* meteorites next to nickel iron.		
Graphite	C.			
Cohenite	$(FeNiCo)_3C$			
Glass.				
Chromite	$FeO.Cr_2O_3$			
Amorphous carbon	C.			
Diamond	C.			
Daubréelite	$FeS.Cr_2S_3$			
Tridymite	SiO_2			
Lawrencite	$FeCl_2$			
Magnetite	Fe_3O_4			4.57 (one meteorite).
Oldhamite	CaS_2			
Hydro-carbons:				
(a) C and H	CH_{2n}			Less than 1 in majority of meteorites in which present.
(b) C, H, and S	$C_4H_{12}S_5$			
(c) C, H, and O	$C_9H_8O_2$			

The list of elements in meteorites given by Farrington[a] includes all those, except fluorine, which compose as much as 0.01 per cent of the outer part of the earth and a number of others. Farrington has given also a list of the eight chief elements in meteorites, including both falls and finds, in order of their abundance (column 1).[b] For comparative purposes there are placed opposite these, in order of abundance, the eight elements which, according to Clarke, are most plentiful in the outer part of the earth (column 2).

[a] Farrington, cit., pp. 393, 394.

[b] Farrington, cit., p. 394.

Order of abundance of elements in meteorites and in the outer rocks of the earth.

Meteorites.	Outer crust of earth.
1. Iron.	Oxygen.
2. Oxygen.	Silicon.
3. Silicon.	Aluminum.
4. Magnesium.	Iron.
5. Nickel.	Calcium.
6. Sulphur.	Sodium.
7. Calcium.	Magnesium.
8. Aluminum.	Potassium.

Nickel and sulphur are found in column 1 and not in column 2, but in the latter sodium and potassium appear. Farrington suggests that because iron meteorites are preserved longer than stony meteorites, and are therefore more likely to be found, iron probably occupies a higher place than it would if meteoric falls only were considered. He further suggests: "The relative excess of magnesium and nickel and scarcity of aluminum and calcium in meteoric as compared with terrestrial matter may be due to the same cause."[a]

REDISTRIBUTION OF THE CHEMICAL ELEMENTS.

We are now prepared to consider the redistribution of the important chemical elements as a joint result of the forces and agents of metamorphism, including therein for this purpose the forces and agents of denudation. In order to appreciate the results it is perhaps well to state the point of view from which the redistribution is considered. If the distribution of any element in the igneous and sedimentary rocks be compared it will be found that in the latter class certain formations are deficient in a given element, and correlative with this deficiency there is a surplus in some other formation or formations. In other words, for any element some sedimentary formations, as compared with the igneous rocks, are likely to show marked deficiencies and some formations marked segregations. Where the material segregated has a value to man, either in the form in which it exists in nature or as furnishing the source of one of the elements, it becomes an economic product. Thus in tracing out the redistribution of the elements we are arriving at the genesis of various economic products. In this chapter only the abundant elements are considered, but where an abundant element may be an ore we are to that extent dealing with the genesis of ore

[a] Farrington, cit., p. 394.

deposits, as for instance in the case of iron. The development of the greater number of ore deposits involves the segregation of the rarer elements, and this aspect of the subject is especially considered in the following chapter.

OXYGEN.

Oxygen is the most abundant of the elements, both in the lithosphere and in the hydrosphere. According to Clarke's estimate of 1891 oxygen composes 49.98 per cent of the lithosphere, hydrosphere, and atmosphere together, or only 0.04 per cent short of the total amount of all the other elements. According to Clarke's estimate of 1891 it composes 47.29 per cent of the lithosphere, and according to his estimate of 1900, 47.02 per cent.[a] Of the hydrosphere it composes 85.79 per cent, and of the atmosphere 23.12 per cent. While the percentage of oxygen in the hydrosphere is greater than in the lithosphere, by far the greater proportion of the oxygen is in the lithosphere, on account of its enormous mass, although an immense quantity is in the hydrosphere. The oxygen of the lithosphere and hydrosphere is combined, while that of the atmosphere is free. Oxygen differs from all of the other abundant elements in that a large quantity of it is in the free state. The only other abundant element which occurs partly in the free state is iron, and the amount of free iron in the lithosphere is exceedingly small. One other element, nitrogen, near the bottom of the list of the 23 more plentiful elements, also occurs in the free state and in even greater quantity than oxygen. Oxygen is the element second in abundance in the meteorites. Among the gases of the meteorites free oxygen is not included in the list given by Farrington, but Wright reports oxygen as occluded.[b] Even if oxygen exists as a gas in meteorites, this is not evidence that this oxygen was brought from the outer space. It may have been absorbed there or while the meteors were passing through the atmosphere, or partly in both ways.

The source of oxygen for the atmosphere is a matter of great consequence, since in the process of oxidation, one of the fundamental processes of the zone of katamorphism, the oxygen is derived directly or indirectly from the atmosphere. So far as known, the vast quantity of free oxygen

[a] Clarke, cit., Bull. 78, p. 39: Bull. 168, p. 15.

[b] Wright, A. W., Spectroscopic examination of gases from meteorites: Am. Jour. Sci., 3d ser., vol. 9, 1875, p. 301.

within the lithosphere is combined, and there is no evidence that this is not true of the centrosphere also.

It might be supposed, as has been suggested by various men in reference to carbon dioxide, that oxygen has been attracted to the earth by the force of gravity from the interplanetary spaces. To what extent this has occurred, if at all, must long, and perhaps forever, be a matter of conjecture.

The chief certain source of oxygen for the atmosphere is the reducing action of organic material upon carbon dioxide. As plants grow they decompose carbon dioxide of the atmosphere, thereby liberating oxygen, and build the carbon into their bodies. Animals take their carbon compounds directly or indirectly from plants. So far as the plants and animals decompose, the carbon is again oxidized to carbon dioxide by the oxygen of the atmosphere, thus consuming an amount of oxygen equivalent to that originally liberated. Therefore, so far as life products decompose there is no permanent gain of oxygen to the atmosphere by the cycle. But a portion of the organic compounds do not completely decompose, and in so far as this is true and they remain in the rocks in carbonaceous shale, graphitic slates, schists, or gneisses, in peat, in coal, and other rocks, the oxygen liberated by the reduction of the carbon dioxide is a permanent gain to the atmosphere. It will be seen under carbon, pp. 962–974, that the quantity of carbon which is thus locked up in the earth is enormous. Since no quantitative estimate has ever been made of the amount of such carbon, there is no way in which one can ascertain to what extent the air has gained in oxygen in consequence of the reduction of carbon dioxide. But it is suspected that a considerable percentage of the oxygen now in the atmosphere could be thus accounted for. Indeed the reduction of carbon dioxide by plants and the liberation of oxygen to the atmosphere in consequence of the formation of the rock coals, peats, etc., has so impressed Koene and Phipson as to make them think that originally the relations of carbon dioxide and oxygen in the atmosphere were probably reversed, but that as a result of the continuous reducing action of vegetation and the decay of only a part of it the atmosphere has become one in which carbon dioxide is very subordinate and oxygen one of the chief constituents.[a]

[a] Chemical News, vol. 67, 1893, p. 135; vol. 68, 1893, pp. 45, 75, and 259; vol. 70, 1894, p. 223.

But the oxidation of carbon and deoxidation through life take into account only one aspect of the question. The inorganic carbon compounds of the original earth stuff should also be considered, and Koene and Phipson ignore this side of the question. It will be seen, under carbon, that this element in various forms is a constituent of the original igneous rocks, and it has been seen that carbon compounds are also constituents of meteorites. So far as elemental carbon, carbon monoxide, carbureted hydrogen, or other carbon compounds are present in the original igneous rocks and have been oxidized to carbon dioxide, demands have been made upon the oxygen of the atmosphere. These demands have certainly been large. No data are at hand to make even an approximate estimate as to how large a quantity of oxygen has thus been abstracted from the atmosphere during geological ages. But, as explained under carbon, the oxidation of carbon compounds of the original igneous rocks is believed to be one of the chief sources of carbon dioxide. In so far as this reaction has taken place it is a reversal of that of vegetation. Which of these opposing processes is preponderant is a question of great importance, but one upon which not even a qualitative guess is warranted. Therefore no statement can be made as to whether the atmosphere has permanently gained or lost oxygen as a consequence of the oxidation and deoxidation of carbon compounds throughout geological time.

A second very important reaction which depletes the atmosphere in oxygen is the oxidation of the ferrous iron of the original rocks. It has been pointed out (Chapters VI and VIII) that oxidation of the ferrous oxide to the ferric oxide is characteristic of the belt of weathering and that the reduction of the ferric oxide to the ferrous oxide may occur in the belt of cementation and is characteristic of the zone of anamorphism. But the oxidation of ferrous iron to the ferric form clearly preponderates over the reduction of ferric oxide to ferrous oxide, and hence oxygen is consumed. This is shown by the following facts:

In 78 shales the percentage ratio between the ferrous oxide and the ferric oxide is 2.46 : 4.03; in 624 sandstones the ratio is 0.57 : 1.24; in 843 limestones the ferrous oxide is so small that it is undetermined, but the ferric oxide is 0.66. Giving these sets of numbers the respective weights of 0.65, 0.30, and 0.05 (the estimated proportions of these different kinds of sediments), the ratio between the ferrous oxide and ferric oxide in the

sediments as a whole is 1.77 : 3.025. The amount of ferrous oxide is about one-half of that of the original igneous rocks, 3.52 per cent. The amount of ferric oxide somewhat exceeds that in the original rocks, 2.63 per cent, but this excess falls far short of the amount required to compensate for the deficiency of ferrous iron in the secondary rocks, for the total amount of iron in 1.77 per cent of ferrous oxide and 3.025 per cent of ferric oxide is 3.49, whereas the total amount of metallic iron existing in the oxidized form in the original rocks is 4.58, the remainder of the 4.64 total iron, as given by Clarke, probably being largely accounted for by the iron united with sulphur. It therefore appears that a large amount of the iron of the original rocks is not accounted for in the sediments which are ordinarily analyzed, and this difference amounts to one-fourth of the total amount of iron in the original rocks. This vast deficiency in iron oxide is probably largely accounted for by the segregation of iron in the iron-bearing formations and in the iron-ore deposits such as those in the Lake Superior region. The iron in these formations is dominantly in the ferric form. Certainly the ratio of ferric oxide to ferrous oxide in them is as great as among the sediments.

Supposing, therefore, that the ratio of ferrous oxide and ferric oxide in the iron-bearing formations is the same as in the sediments analyzed, and increasing the amounts of ferrous oxide and ferric oxide in the shales, sandstones, and limestones together in the same ratio, so that they contain an amount of iron equivalent to that in the original igneous rocks, thereby including the iron-bearing formations, this would give 2.35 per cent of ferrous oxide and 4.02 per cent of ferric oxide. Upon this hypothesis the difference between the amount of ferrous oxide present in the original rocks, 2.35 per cent, and that now found upon the average in the secondary rocks, 1.77 per cent, is 0.58 per cent. To change this percentage of ferrous oxide to ferric oxide for the 675,000,000,000,000,000 metric tons of sediments of the zone of katamorphism would require 435,000,000,000,000 metric tons of oxygen, or 35.55 per cent of the oxygen now in the atmosphere. (See p. 944.) This shows how enormous has been the draft of oxygen from the atmosphere in consequence of the oxidation of ferrous oxide alone. (See p. 1003.)

Another very large demand upon oxygen is made by the oxidation of the metals and the sulphur united as sulphides in the original rocks. Of the

metals united with sulphur, iron of course dominates over all others combined. We may therefore use FeS_2, the most common sulphide, to illustrate the process. If the iron were changed to the ferric oxide and the sulphur to sulphuric acid, the reaction may be represented by the equation—

$$2FeS_2+15O+4H_2O=Fe_2O_3+4H_2SO_4.$$

Since sulphates are not known in the original igneous rocks, nor in meteorites, it is to be presumed that practically all the sulphates which now exist are a result of the oxidation of the sulphur of the sulphides by oxygen. The total amount of sulphates in the ocean is vast. The amount of sulphur present as sulphates in the ocean is estimated by Dittmar to be 1,187,000,000,000,000 metric tons. The oxygen derived from the atmosphere to unite with this sulphur in order to produce sulphuric acid is 1,777,200,000,000,000 metric tons, or 145.25 per cent of that now in the atmosphere. If the sulphur in the sulphate deposits be estimated as equal to one-tenth that in the ocean, the amount of oxygen required for the production of all the sulphates would be 159.77 per cent of that now in the atmosphere. As shown by the above equation, to oxidize the iron of sulphides to the ferric oxide requires one-fourth as much oxygen as the oxidation of the sulphur to sulphuric acid. Thus for this part of the process 39.94 per cent of the amount of oxygen in the atmosphere would be required. Summing all these amounts we find that for the oxidation of the sulphides 2,443,473,000,000,000 metric tons of oxygen, or 199.91 per cent (i. e., twice), that now in the atmosphere, has been consumed. (See p. 1003 for possible modification.)

It is shown elsewhere that sulphates produced by oxidation of the sulphides are extensively reduced to sulphides by carbonaceous material, and this cycle of reproduction of sulphates and sulphides for some of the material doubtless has been repeated many times. The above is a first attempt to roughly estimate the amount of oxygen required to produce the present existing sulphates, not the total amount of oxygen which has been consumed in the oxidation of the sulphides to sulphates through geological time. So far as the sulphides have been changed to sulphates and reduced again to sulphides by organic matter, a consideration of the amount of oxygen which is drawn from the atmosphere by this process has already been accounted for in considering the relations of oxygen and carbon.

Metallic iron is known as a rare constituent of certain very basic igneous rocks. When such material reaches the zone of katamorphism the iron is oxidized to ferrous oxide or ferric oxide, and thus oxygen is consumed. At the present time the consumption of oxygen by metallic iron is so small as to be insignificant, but it is possible that earlier in the history of the earth, before the segregation of the oxidized products at the surface, not only iron, but possibly other metals, may have been oxidized in great quantity, and thus enormous quantities of oxygen abstracted from the atmosphere. The quantity of oxygen which has thus been consumed must, so far as one can see, ever be a matter of conjecture.

The source of the water of the hydrosphere is uncertain. It may be supposed that early in the history of the earth a large part of the elements composing water was in a free state, although doubtless a part was also combined. If any considerable proportion of the water of the hydrosphere was produced by the oxidation of hydrogen during the time the sedimentary rocks were deposited, the amount of oxygen thus consumed would have been enormously greater than that required for the processes which have heretofore been considered, indeed, many times greater than the amount of oxygen now in the atmosphere. However, it is useless to speculate as to the extent to which the oxidation of hydrogen took place in early geological time. It is probable that during the deposition of the sedimentary rocks, and even at the present time, hydrogen is being oxidized on a small scale. It is seen (pp. 945–946) that hydrogen and carbureted hydrogen are constituents of meteorites, and further that hydrogen occurs occluded in various rocks. Hydrogen is met also in connection with fumarolic and solfataric action. As already explained (p. 492), this hydrogen is supposed to be produced by the reaction of the ferrous oxide upon water, according to the equation

$$H_2O+2FeO=2H+Fe_2O_3.$$

So far as water is produced by the oxidation of hydrogen free or combined oxygen is abstracted from the atmosphere. This abstraction certainly occurs to some extent in volcanic districts. Phipson also holds that hydrogen, so far as it is present in the atmosphere, may be oxidized by the nascent oxygen freed by plants. He grew certain plants in an atmosphere of hydrogen and was thus able, as he claims, to completely oxidize all of it.[a]

[a] Phipson, T. L., Vegetation in hydrogen: Chemical News, vol. 67, 1893, p. 303.

It might be supposed that in counting the oxygen consumed in the oxidation of hydrogen to produce water, that formed by the decomposition of water through the agency of ferrous oxide should be disregarded, since the amount of oxygen required for the change of ferrous oxide to ferric oxide in the change from the original to the altered sediments has already been estimated. But the lavas are original igneous rocks and the ferric oxide which they contain may be in part produced by the oxidation of ferrous oxide through water in accordance with the equation above given, and therefore the oxygen required to oxidize the ferrous oxide to the ferric oxide as calculated (p. 951) does not include that required by the reaction above.

Since there is so little hydrogen in the air, it might be argued that the oxidation of hydrogen has taken place upon the earth on a great scale, and therefore that large quantities of oxygen have been thus consumed. But Chamberlin has shown that it is doubtful if hydrogen can be permanently held in the atmosphere by the attraction of the earth.[a] If free hydrogen can escape from the earth it can not be assumed that the amount of oxygen required to oxidize hydrogen is important, at least during later geological time.

Another way in which oxygen has been consumed by metamorphism is in the oxidation of nitrogen. It has been explained (pp. 465–466) that in various ways, but chiefly by means of the bacteria and leguminose plants, free nitrogen is oxidized to nitric acid, and in consequence the nitrates are formed. Since the nitrates are not known in the original igneous rocks, nor in meteorites, it is to be presumed that all of the nitrogen compounds upon the earth have been produced by the oxidation of nitrogen. At the present time it is wholly impracticable to make any estimate of the amount of nitrates upon the earth. In arid regions, as is well known, there are large deposits of nitrates. (See p. 787.) In some humid regions, as for instance at places in the Orinoco Basin of South America, the nitrates compose a large percentage of the soil. As explained (pp. 505–506), nitrates are essential constituents of all fertile soils. Hence, while no quantitative statement can be made, the quantity of oxygen which must have been consumed in the oxidation of nitrogen must have been very large.

[a] Chamberlin, T. C., A group of hypotheses bearing on climatic changes: Jour. Geol., vol. 5, 1897, pp. 666–667.

Besides the compounds already considered there are various rarer substances which have been oxidized, such as manganous oxide. Doubtless, however, the consumption of oxygen by the rarer compounds is inconsiderable.

The above calculations may be only roughly approximate, but they seem to show that the amount of oxygen which has been abstracted from the atmosphere during geological time in the oxidation of iron and sulphur is enormous—apparently about twice that now free in the atmosphere. If these results be correct, omitting any consideration of the amount which has been required for the oxidation of hydrogen, nitrogen, and other substances, the original atmosphere must have been much more voluminous than at present, or else during geological time there has been some source of oxygen from which the atmosphere has been replenished.

In the previous pages only the sediments of the zone of katamorphism are considered. While in the zone of katamorphism oxygen has been added to the lithosphere and abstracted from the atmosphere, it is equally certain that in the zone of anamorphism and in the belt of cementation deoxidation takes place to some extent. Reduction is usually accomplished through vegetation, carbon being oxidized at the same time and largely returned to the atmosphere as carbon dioxide. So far as this is the case it involves no correction beyond that already considered, since the end result is the same as if this carbon had been oxidized by the process of decomposition at the surface of the earth, and thus to that extent balanced the process of liberation of oxygen when the organic carbon compounds were originally formed. On the whole there is no reason to believe that the sedimentary rocks metamorphosed in the zone of anamorphism contain more ferric oxide than the original rocks. Until the relative amounts of ferrous and ferric oxides in the sedimentary rocks of the zone of anamorphism are compared with the amounts of these compounds in the original rocks, it can not be asserted whether the sum total of the reactions of the sedimentary rocks in the zone of anamorphism is in the direction of the consumption or liberation of oxygen.

The oxygen added to the zone of katamorphism is not uniformly distributed, but is segregated to a very large extent. The most important segregation is that occurring in connection with iron. There are vast quantities of ferric oxide in the red sandstones, and the added oxygen is

therefore distributed through these. A much greater concentration of the added oxygen is, however, found in the rich and lean iron-ore formations, from the Archean to the Pleistocene. Such segregation is well illustrated by the Clinton iron ores, and is shown on a magnificent scale by the ferruginous formations of the Lake Superior region. The gypsum and nitrate deposits, aside from the iron, are those in which the oxygen abstracted from the atmosphere is segregated to the greatest extent.

In summary it appears that the chief certain source of oxygen for the atmosphere is the reduction of carbon dioxide by vegetation and the burial of a part of this vegetation in the earth. This source is vast in amount.

On the other hand, oxygen has been consumed by the oxidation of the carbon compounds of various kinds in the original igneous rocks and in the meteorites; by the oxidation of ferrous oxide to ferric oxide in the zone of katamorphism; by the oxidation of iron in the metallic form and as a sulphide; by the oxidation of sulphur, nitrogen, and hydrogen; and in some small measure by the oxidation of rarer compounds, such as manganous oxide. The sum of these gives the amounts of oxygen consumed during geological time. Until estimates have been made of the various amounts of the oxidized compounds, it is wholly out of the question to make any quantitative estimate of the total amount of oxygen which has been abstracted from the atmosphere by the process of oxidation since the beginning of geological time, but it is certain that the amount of oxygen thus consumed has been enormous. It probably vastly exceeds the amount of oxygen which has been liberated to the atmosphere by the reduction of carbonic acid through plants.

If this conclusion be correct such wild guesses as those of Koene and Phipson (see p. 949), that the carbon dioxide of the original atmosphere greatly exceeded the oxygen and that the proportions of these elements have been reversed in consequence of the reduction of carbon dioxide by organic matter, are wholly unwarranted. This case illustrates the danger of drawing a conclusion from the consideration of only one factor of a complex problem.

SULPHUR.

According to Clarke's estimate of 1891 sulphur forms 0.04 per cent of the outer 10 miles (16.1 kilometers) of the earth, including the original rocks, hydrosphere, and atmosphere, 0.09 per cent of the ocean, and 0.03 per cent of the original rocks. However, in his estimate of 1900 the amount in the original rocks is increased to 0.07 per cent. Sulphur thus has fourteenth place in the scale of abundance.[a] If the sulphur were reckoned as contained in SO_3 Clarke's estimates for 1891 and 1900 for the original rocks would be 0.0749 and 0.1748, respectively.

It is well known that sulphides are constituents of the original igneous rocks. Sulphur occurs in these rocks as pyrite and pyrrhotite certainly. Sulphur is found also in the meteorites in the form of troilite (FeS), possibly as pyrrhotite (Fe_nS_{n+1}), as oldhamite (CaS_2), and also in the hydrocarbon ($C_4H_{12}S_5$). It thus appears that there are various sources of sulphur in the material of which the earth is formed.

Sulphur occurs in the shales, sandstones, and limestones as sulphates and sulphides. The amount of SO_3 reported by Clarke in 78 shales is 0.65 per cent; in 624 sandstones, 0.08 per cent. No sulphur as sulphide is reported, but Clarke writes that the above determinations include probably both the sulphur as sulphate and as sulphide. The amount of SO_3 in 843 limestones is 0.06 per cent, and the amount of sulphur as sulphides in these limestones is 0.08. The latter amount corresponds to 0.20 per cent SO_3, and thus if all of the sulphur of the limestones were reckoned as SO_3 the amount would be 0.26 per cent.

It thus appears that, taking into account the molecular weights of sulphur and SO_3, sulphur is about four times as abundant in the shales as in the original rocks, is reduced by about one-half in the sandstones, and is increased by about one-half in the limestones. Since the volume of the shales is so great, the amount of SO_3 in the shales is much more than sufficient to compensate for the deficiency in the sandstones even if the excess in the limestones were ignored. If one were to combine amounts of sediments and percentage of SO_3 in these rocks, and thus make an estimate of the amount of the compound there should be in the original rocks, he would have the following equation:

$$.65\times.65+.08\times.30+.26\times.05=.4595$$

[a] Clarke, cit., Bull. 78, p. 39; Bull. 168, p. 15.

Clarke's average for the original rocks is 0.1748. It thus appears as if there were an excess of sulphur in the secondary rocks amounting to 0.2847 per cent. To this excess, upon the theory that the salts of the ocean have been derived from the original rocks, should be added the vast amount of SO_3 in the ocean. Reckoned as sulphur, from Dittmar's estimates this is 1,187,000,000,000,000 metric tons, which corresponds to 2,964,000,000,000,000 metric tons of SO_3. But this is only .439 per cent of the total mass of the sediments.

The above calculations as to the amount of SO_3 in the sediments take no account of gypsum deposits. If these be supposed to contain one-tenth as much SO_3 as the ocean, namely, .0439 per cent of the total amount of sediments, there is in the sediments and the ocean together an excess of .7676 per cent beyond the amount calculated in the original rocks.

These facts show that there is a great discrepancy between Clarke's estimate of 0.1748 per cent of SO_3 in the original igneous rocks and the amount of sulphur in the secondary rocks. It is thought highly probable that this discrepancy is largely explained by the actual escape of much sulphur as a gas during periods of volcanism, as hydrogen sulphide, which is oxidized during volcanic action, or by the direct oxidation of the sulphur to SO_2 or SO_3. It is certain that the amount of sulphur may be greater in the secondary than in the original rocks, as is shown by analyses, because the original rocks contain only the residual sulphur which separated as a sulphide when the magma crystallized. While the igneous rocks may lose a considerable portion of their sulphur before crystallization, this may not fully explain the discrepancy. It is possible of course that Clarke's estimate of sulphur in the original igneous rocks may be somewhat too small, since this element is in such subordinate amount, and selections for analysis were made upon the basis of other elements rather than to get an average sample for sulphur.

As to the geological processes through which the redistribution of the sulphur takes place, the following summary statement may be made: In the alteration of the original rocks in the belt of weathering, the sulphides are largely oxidized to sulphates, which are for the most part taken into solution by the underground waters. Some of this dissolved material is carried down into the belt of cementation, and a portion is there precipitated as sulphate in the form of barite, celestite, and gypsum; another part is again

reduced to sulphide by organic matter and other reducing agents, and in this form is precipitated. These precipitates are mainly those of the heavy metals, especially of iron. A considerable portion of the sulphates which form in the belt of weathering and are carried to the belt of cementation is brought to the surface by solutions which join the overground circulation. By this circulation sulphates are transported to the sea. It has already been noted that a large amount of sulphur is found in the sea as sulphate. The amount now present in solution is not necessarily any measure of the amount which has been contributed to the ocean. Indeed the relatively large amount of sulphates in the shales suggests that where immense masses of mud have become mingled with the sea water, as at the mouths of great rivers, reactions take place which result in the precipitation of the sulphates, and these salts thereby become mingled with the muds which later are transformed to shales. While by far the larger portion of the sulphates of the overground circulation are carried to the sea, in areas such as the Great Basin calcium sulphate is thrown down in the lakes and gypsum deposits are built up. Such deposits are of very considerable magnitude. So far as these gypsum deposits formed in the zone of katamorphism pass into the zone of anamorphism they may become dehydrated and anhydrite be formed.

Gypsum and barite are of very considerable economic importance in various ways. In these products a very large amount of sulphur is concentrated. The segregated sulphur, which, combined with the other elements, makes these products of value, has been brought together in the condensed form from the fraction of 1 per cent of the sulphur in the original rocks. Thus we have another illustration of the manner in which processes of metamorphism segregate elements, and result in the formation of deposits which are of service to man.

SILICON.

Silicon stands second in abundance among the elements of the earth. According to Clarke's estimate of 1891 silicon forms 25.30 per cent of the lithosphere, hydrosphere, and atmosphere together, and of the lithosphere alone 27.21 per cent, a little more than one-fourth of the total. According to Clarke's estimate of 1900 silicon composes 28.06 per cent of the lithosphere.[a] All of this silicon is combined. In analyses silicon is usually

[a] Clarke, cit., Bull. 78, p. 39; Bull. 168, p. 15.

reported with its combined oxygen as silica. Stated as silica, Clarke's estimates of 1891 and 1900 are 58.59 and 59.71 per cent, respectively.[a] This is the average, and in the original rocks the silica rarely falls below 50 per cent and rarely rises above 75. Of the elements present in meteorites it has been seen that silicon is third in abundance. Much the larger portion of the silicon in the original rocks occurs as silicates, although a large amount occurs as silica in quartz.

The amount of silica in 78 shales is 58.38 per cent, in 624 sandstones is 81.76 per cent, and in 843 limestones is 9.64 per cent. (See p. 938).

It is plain from the foregoing that within the lithosphere metamorphism, denudation, and sedimentation have redistributed the silica to a very important extent. In the shales the amount remains about the same as the average for the original rocks. In the limestones the amount of silica has been very greatly reduced; indeed, to less than one-sixth of that in the original rocks. Complementary to this depletion of silica in the limestones is its segregation in the sandstones. In these rocks the silica is a little more than one-third greater than the average for the original rocks. This small difference is due to the fact that the silica in the sandstones is mainly in the form of quartz; while in the original rocks, as already noted, the larger part is in the silicates, of which it composes about two-thirds. Therefore, while the percentage of silica in the lithosphere as a whole is two-thirds as great as in the sandstones, the amount of silica as quartz in the lithosphere, 12 per cent (see p. 937), is only about one-sixth as great as in the sandstones, for the majority of sandstones contain 75 per cent or more of silica.

Considering the zone of katamorphism, there is constant solution of silica in the belt of weathering and steady additions of silica in the belt of cementation, already fully explained. (See pp. 473–480, 516–517, 621–623, 634–636.) Carbonation in the belt of weathering destroys the silicates and liberates silica as colloidal silicic acid. This is largely carried downward into the belt of cementation and is there deposited in enormous quantities. (See p. 618.) Hence we have constant subtraction of silica from the belt of weathering and its steady addition to the belt of cementation. In the belt of weathering the proportion of silica may be increased or decreased according to the rate of solution of the other elements. (See pp. 507 et seq.).

[a] Clarke, cit., Bull. 168, p. 14.

By erosion the belt of cementation, enriched in silica, rises into the belt of weathering and the rocks rich in quartz are broken down. The larger part of the quartz is not chemically modified, but mechanically disintegrated, contributed to the streams, and by them carried to the sea. It there joins the quartz liberated from the rocks of the shore by the action of the waves, and the whole is segregated in sandstone formations. Many of the sandstone formations thus produced in early geological time later became land areas. During later geological time streams running over sandstone areas contributed to the sea more than an average amount of quartz. Thus the combined processes of metamorphism and denudation have resulted in segregating sufficient quantities of quartzose sands to produce the quartz-sand formations and their metamorphosed equivalents, the quartzites and quartz-schists.

In the deep-seated zone of anamorphism silica is neither added nor subtracted in any considerable quantity, but the form of the compound is often extensively changed. As fully explained (pp. 677–679), silica unites with the bases, especially those of the carbonates, to produce silicates. Whether at the present time the destruction of the silicates in the zone of katamorphism, and especially in the belt of weathering, or the development of the silicates and the destruction of the carbonates in the zone of anamorphism is more important is considered under the heading "Carbon." (See pp. 962–974.)

The proportion of silica in the different classes of sediments gives a criterion by which the estimates of the relative amounts of the sediments (see pp. 940–941) may be very roughly tested. If the shales, sandstones, and limestones compose 0.65, 0.30, and 0.05 of the sediments, respectively, and contain the percentages of silica above given, the sum of the multiples of the percentage of silica in each of the sediments by the quantities of the sediments should equal the average percentage of silica in the original rocks. Thus

$$58.38\times.65+81.76\times.30+9.64\times.05=62.957.$$

But this equation shows an excess of 3.247 per cent of silica over that determined by analysis, 59.71 per cent.

Practically all of the silicon occurs in the lithosphere. If all classes of sedimentary rocks were taken into account, including both their composition and mass, an estimate of the percentage of silica based upon the sediments

ought to correspond with the percentage found in the original igneous rocks. Therefore the discrepancy above noted indicates that there are factors left out of and errors in the above equation. In reference to the similar equations of most of the other elements it will be seen that the determination of the amount of the element as made from the sediments usually shows a deficiency as compared with the original rock. It will be explained that one of the reasons for this is that determinations of the average composition of the sedimentary rocks based upon analyses of the shales, sandstones, and limestones neglect the particular formations in which an element is segregated to the largest extent. In the case of silica the reverse is the case. The sandstones in which silica is concentrated are included; whereas other exceptional compounds in which there is depletion of silica are not included. Consequently we should expect in the case of this compound that the estimates made upon the basis of the sediments should be in excess of the amount found in the original igneous rocks. While the discrepancy is thus partly explained, I suspect that it is due more largely to an error in the determination of the amount of silica in the shales. Few analyses have been made of this class of compounds. It will be seen on subsequent pages (see pp. 984–986) that alumina shows a discrepancy just the reverse of that of silica. It appears to me probable that when we have better representative analyses of the shales, taking into account their composition and masses, the silica will be lower and the alumina higher than in the analyses given.

CARBON.

AMOUNT OF CARBON.

In 1891 Clarke estimated the carbon as 0.21 per cent of the lithosphere, hydrosphere, and atmosphere together. This corresponds to 0.22 per cent of the original rocks, 0.002 per cent of the hydrosphere, and only .0127 per cent by weight of the atmosphere. In 1900 his estimate for the lithosphere was reduced to 0.12 per cent. Recently Letts and Blake,[a] as a result of careful consideration of all the data and new work, conclude that carbon dioxide is present in the atmosphere to the amount of three volumes in 10,000, which corresponds to about 0.045 per cent by weight.[b]

[a] Letts, E. A., and Blake, R. F., The carbonic anhydride of the atmosphere: Sci. Proc. Royal Dublin Society, vol. 9, new series, pt. 2, 1900, p. 172.

[b] Mendeléeff, D., The principles of chemistry, translated by George Kamensky: Longmans, Green & Co., London, 6th ed., 1897, vol. 1, p. 238.

Reckoned as an oxide, 0.12 and 0.22 per cent of carbon would correspond to 0.44 and 0.81 per cent of carbon dioxide, respectively. This places carbon dioxide tenth among the oxides, and carbon eleventh in abundance, making it less plentiful than either hydrogen or titanium. In Clarke's estimate of 1900 the carbon in limestones is excluded from consideration.[a] In his estimate for 1891 is included the carbon in a layer of limestone 528 feet thick enveloping the globe, the amount of limestone estimated by Reade.[b]

When Clarke made his estimate in 1891 he thought the analyses of volcanic and crystalline rocks probably showed too high a percentage of carbon dioxide, since the rocks analyzed were not perfectly fresh. But he regards this error as offset by the undeterminable amount of carbon in coals, shales, and petroleums, which were not considered.[b] He thinks his resultant estimate, 0.22 per cent for the lithosphere, can hardly be too low. However, it is possible that this estimate is too small, since it is practically impossible to make more than the roughest sort of a guess as to the amount of carbon contained as graphite, anthracite, and hydrocarbons in the crust of the earth. The quantity of carbon in the coal of the earth has never been estimated, and doubtless the quantity present in workable beds is less than that present in nonworkable, widely extended, small, and thin seams. Furthermore, in the carbonaceous shales associated with the coals there is a vast amount of carbon, possibly more than in the coals. Shales as old as the Algonkian in some places contain nearly 20 per cent carbon. Graphitic gneisses have a widespread occurrence among the older metamorphosed sediments. It seems to me that the carbon present in the above forms in the lithosphere is likely to much more than compensate for the excess of carbon dioxide due to alteration in the igneous and crystalline rocks analyzed, since rocks which are as fresh as can be obtained are always selected for analysis. But, on the other hand, the estimated amount of carbon in limestone is probably too high, for it is very probable that Reade's estimate of the quantity of limestone is too great. While it is possible that the amount of carbon in the lithosphere is somewhat greater than the larger amount estimated by Clarke, even interpreting all doubtful points in favor

[a] Clarke, F. W., Bull. U. S. Geol. Survey, No. 168, p. 15.
[b] Clarke, Bull. U. S. Geol. Survey, No. 78, p. 38.

of carbon, the amount would still be small, certainly but a fraction of 1 per cent.

Farrington's[a] analyses of meteorites show that carbon is present in these bodies in various forms. As a solid it occurs as amorphous carbon, as graphite, and as diamond. As solid hydrocarbons it is found as CH_{2n}, as $C_4H_{12}S_5$, and as $C_9H_8O_2$. As gases included in the meteorites it occurs as carbon monoxide (CO), carbon dioxide (CO_2), and carbureted hydrogen (CH_4). The total quantity of all of these compounds in any one meteorite is small, usually less than 1 per cent, and corresponds very well with the amount in the outer 10 miles of the earth.

The importance of carbon compounds to the lithosphere is out of all proportion to the abundance of this element. As is well known, the carbon compounds are the basis of all forms of life, and it has been seen that life is one of the most potent factors concerned in the decomposition of rocks. Hence the small percentage of carbon in the lithosphere, hydrosphere, and atmosphere is of first importance among the elements concerned in the metamorphism of rocks.

SEGREGATION OF CARBON.

It is evident from what has been said in considering the amount of carbon in the lithosphere that this element has been segregated in various ways. Carbon is segregated (1) by the process of carbonation, and (2) in the carbonaceous deposits. It has been seen (pp. 473–474) that the carbon now being segregated is directly derived from the carbon dioxide of the atmosphere. The amount of CO_2 in the atmosphere, calculated upon the basis of 0.045 per cent by weight, is 2,381,400,000,000 metric tons. This figure is very close to that of Dittmar, who estimates the amount to be 2,277,000,000,000 metric tons.[b] Each of the processes of segregation and the sources of supply of carbon dioxide to the atmosphere will be considered.

Segregation by carbonation.—Many years ago Hunt[c] stated "that the carbonic acid absorbed in the process of rock-decay during the long geologic ages, and now represented in the form of carbonates in the earth's crust, must have equalled probably two hundred times the entire volume of the present

[a] Farrington, cit., pp. 395–408, 522–532.

[b] Dittmar, William, Narrative of the cruise of H. M. S. *Challenger*, 1873–1876, vol. 1, pt. 2, 1885, pp. 954–955.

[c] Hunt, T. Sterry, The geological relations of the atmosphere: Rept. British Assoc. Adv. Science, 1878, p. 544.

atmosphere of our earth." The data upon which this calculation is made are not given, and it may be a great overestimate, but that any calculation could have given such a result shows how trivial is the amount of carbon dioxide at present in the atmosphere as compared with that which has been abstracted by carbonation.

In 78 shales the amount of carbon dioxide is 2.64 per cent, in 624 sandstones it is 3.03 per cent, and in 843 limestones it is 38.58 per cent.

While segregation of the carbonates is therefore the rule for all the rocks produced by the processes of denudation, this segregation takes place to the least extent in the shales, to a greater extent in the sandstones, and to the greatest extent in the limestones.

If carbon dioxide composes but 0.81 per cent of the original rocks, it appears that as compared with the average of the original rocks about three times as much carbon dioxide is concentrated in the shales where it is lowest, and forty-seven times in the limestones. This shows how enormously the carbon in the secondary rocks has been increased, as compared with the original rocks, by the process of carbonation in the zone of katamorphism.

Combining the above figures with the masses of the sediments given on page 940, it follows that the amount of carbon dioxide in the shales is 11,583,000,000,000,000 metric tons, in the sandstones is 6,135,750,000,000,000 metric tons, and in the limestones is 13,020,750,000,000,000 metric tons; total, 30,739,500,000,000,000 metric tons. From the foregoing figures it appears that the fixed CO_2 in the shales, sandstones, and limestones is 12,900 times the amount now in the atmosphere, and is 1,970 times the amount of free CO_2 in both atmosphere and hydrosphere, upon the basis of 0.001 per cent in the hydrosphere, and is 660 times the total free carbon dioxide of the atmosphere and the hydrosphere together, upon the basis of Dittmar's figures.[a]

It appears from the foregoing that in the great limestone deposits a large quantity of carbon dioxide, 38.58 per cent, has been segregated from the exceedingly small amount of carbon in the original igneous rocks and from the atmosphere and hydrosphere. As already seen there is 47 times as much carbon in the limestone formations as in the original igneous rocks. The importance of this process of segregation, considered from an economic point of view, is not generally appreciated. In order to realize

[a] Dittmar, Narrative of the cruise, etc., p. 955.

this it is necessary to consider the relations of man to agriculture. The limestone soils of the United States, and of many other parts of the world, are of surprising fertility. The historian tells how settlement followed the limestone soils of the Great Valley, of the Blue Grass region of Kentucky and Tennessee, and of the Upper Mississippi Valley. The world over, limestone soils have unsurpassed fertility. Since the products of the soil are the materials of most importance to man, the greatest geologic formation from an economic point of view is limestone produced by the segregation of carbon and calcium.

Segregation in carbonaceous deposits.—Besides the carbon which is segregated as carbon dioxide in the lithosphere by carbonation, vast quantities have been buried in the rocks in forms varying from nearly pure carbon, as graphite and anthracite, to cellulose. Various estimates have been made of the amount of carbon in the better-known coal beds, but so far as I know no attempt has been made to estimate the amount of carbon in all the coals, good and poor, in the carbonaceous shales associated with them, and in the shales and other rocks not associated with coal beds. The fact that carbon as hydrocarbons exists in shales has been usually overlooked. Carbon forms 0.81 per cent of 78 rocks analyzed. (See p. 938.) This quantity seems small, but when the enormous mass of the shales is considered, 438,750,000,000,000,000 metric tons, it is seen that this percentage amounts to 3,553,875,000,000,000 metric tons. If this amount of carbon were oxidized to CO_2 it would represent 5,470 times the amount of carbon dioxide in the atmosphere, as calculated above. If it could be consumed at the rate of 1,000,000,000 metric tons per year, which is more rapid than the present rate of combustion of coal, it would last over 3,500,000 years. This great amount of carbon, in these, as well as in some other rocks, is ordinarily overlooked. It is therefore certain that the total amount of carbon contained as hydrocarbons in rocks of all kinds, from the great coal seams to the sediments containing but a very small percentage, is enormous.

Next to the limestones the economic product of vastly greater importance than any other is coal. Coal contains on an average 80 per cent carbon, or 364 times the amount in the original igneous rocks, in which the carbon amounts to only 0.22 per cent. The inestimable economic value of coal is so fully appreciated that it need not be emphasized. The point to be understood is that the forces and agents of geology have segregated this immeasurably valuable material from a fraction of 1 per cent of

carbon in the original rocks and from the atmosphere and hydrosphere. Furthermore, the segregation of carbon from widely dispersed material is essential to life, and life has profoundly modified many geological processes. The segregation of carbon by the various geological processes in limestone, in organisms, and in coal explains the great importance of this sparse element in the genesis of the earth.

SOURCES OF SEGREGATED CARBON.

It has been seen that fixed carbon exists in the salts of the ocean and in the lithosphere as a carbonate and as hydrocarbons. The important processes now producing these various carbon compounds are those involved in the interaction of the carbon dioxide of the atmosphere, of organic bodies, and of the rocks. If we apply the fundamental hypothesis of geology that the processes now at work explain past results, we must assume that the carbon dioxide for carbonation and that for the carbonaceous deposits is derived indirectly from the atmosphere. It has been seen that the amount of carbon required for this work is many thousands of times the amount of carbon dioxide now free in the atmosphere, and many hundred times the amount free or potentially free in the hydrosphere. The amount of carbon dioxide in the atmosphere may have been originally vastly greater than at present, but even if this were so the demands upon carbon have been so great that it is probable that the atmosphere has been replenished in that compound. There are several possible sources of carbon dioxide for the replenishment of the atmosphere.

An important immediate source of carbon dioxide is the ocean. The amount of carbon dioxide in the hydrosphere, computed on the basis of a content of 0.002 per cent of carbon (Clarke's estimate), is 96,531,915,000,000 metric tons. Dittmar's estimate of the entire carbon dioxide of the ocean is 70,350,160,000,000 metric tons, or considerably less than Clarke's. Of Dittmar's total he estimates the loose carbon dioxide (i. e., the excess of carbon dioxide of bicarbonates above that required for normal carbonates and the free carbon dioxide together) of the ocean to lie between 35,200,000,000,000 and 52,800,000,000,000 metric tons. Supposing the true amount to be the average of these, this would give 44,000,000,000,000 metric tons or 19.3 times the amount of carbon dioxide in the atmosphere as calculated by Dittmar.[a] According to Schloesing the carbon dioxide

[a] Dittmar, William, Report of voyage of H. M. S. *Challenger*, 1873–76; Narrative of the cruise, vol. 1, pt. 2, 1885, pp. 954–955.

in the bicarbonates of the ocean beyond that required to balance the bases as normal carbonates is about ten times the amount in the atmosphere. It thus appears that the potentially free carbon dioxide of the ocean is in much greater amount than the actual free carbon dioxide in the atmosphere. According to Schloesing[a] there is a very delicate adjustment between the amount of carbon dioxide in the atmosphere and the hydrosphere. Great additions to the amount in the atmosphere would result in absorption by the hydrosphere. Depletion in the amount in the atmosphere is compensated by additions from the hydrosphere. This idea of the balance between the amount of carbon dioxide in the atmosphere and that contained as bicarbonate in the ocean has been elaborated by Chamberlin and Tolman.[b] They note that under the laws of physical chemistry, when the amounts of free carbon dioxide in the atmosphere and in the ocean are in equilibrium and this equilibrium is disturbed by a decrease of the carbon dioxide of the amosphere, this compound will pass from the ocean to the atmosphere until the equilibrium is restored. Chamberlin has also emphasized the fact that when the calcium bicarbonate of the ocean is precipitated by organisms, one-half of the carbon dioxide is thereby liberated. Consequently at periods of limestone building the amount of free carbon dioxide in the ocean, and therefore the amount in the atmosphere, would be greatly increased. These considerations lead to the conclusion that at various times in the history of the world the atmosphere has been replenished in carbon dioxide at the expense of the ocean.

Petrographic work of recent years shows that graphite and diamond are original constituents of some of the igneous rocks, especially the basalts. Further, Tilden,[c] by chemical analyses, has shown that the plutonic igneous rocks granite and gabbro, and also the volcanic igneous rock basalt, at certain localities contain considerable quantities of carbon monoxide and methane.

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[a] Letts, E. A., and Blake, R. F., The carbonic anhydride of the atmosphere: Sci. Proc. Royal Dublin Society, vol. 9, new series, pt. 2, 1900, pp. 160–161.

[b] Chamberlin, T. C., A group of hypotheses bearing on climatic changes: Jour. Geol., vol. 5, 1897, pp. 653–683. Chamberlin, T. C., The influence of great epochs of limestone formation upon the constitution of the atmosphere: Jour. Geol., vol. 6, 1898, pp. 609–621. Chamberlin, T. C., An attempt to frame a working hypothesis of the cause of glacial periods on an atmospheric basis: Jour. Geol., vol. 7, 1899, pp. 545–584. Tolman, C. F., The carbon dioxide of the ocean and its relations to the carbon dioxide of the atmosphere: Jour. Geol., vol. 7, 1899, pp. 585–618.

[c] Tilden, W. A., On the gases inclosed in crystalline rocks and minerals: The Chemical News, vol. 75, 1897, pp. 169–170.

The igneous rocks containing the carbon compounds may flow out in the belt of weathering, or, if deep seated, may reach it by denudation. In either case, under favorable conditions, oxygen may slowly oxidize the amorphous carbon, graphite and diamond, carbon monoxide, and the carbon of methane, to carbon dioxide. If the theory be correct which regards high temperature and volcanism as much more prevalent in the early stages of the earth than at the present time, the oxidation of these compounds may have gone on more rapidly than at present, but even now when lavas containing carbon compounds are poured out over the surface their high temperature in the belt of weathering affords conditions very favorable for the oxidation of the carbon.

In this connection it should be recalled that carbon dioxide is given off in great quantities by volcanoes. "Cotopaxi, according to Boussingault, evolves more carbonic anhydride annually than a whole city like Paris."[a] Cotopaxi is, of course, only a single volcano, and many other volcanoes are giving off large amounts. Moreover, at times of regional volcanism it is to be presumed that vastly more carbon dioxide is given off than at times of local volcanism like the present. It is probable that some, perhaps much, or even a large part of the carbon dioxide extruded by volcanoes is that resulting from the oxidation of the various carbon compounds present in the original magmas, although a part of it may be occluded carbon dioxide and some or much of it may be derived from carbonate formations representing previous segregations.

It is to the oxidation of the carbon of the original rocks that we must look for one important primal source of carbon dioxide.

Tilden found that in a number of rocks, including gneiss, granite, gabbro, and basalt, the volume of occluded gases varied from one to eighteen times the volume of the rock, and of these gases carbon dioxide was the most abundant, varying in five cases from 23 to 78 per cent, but in one case being as low as 5.5 per cent.[b] Occlusions occur even to a greater extent in the sedimentary rocks which have been metamorphosed under deep-seated conditions by the process of silication of the carbonates. When the rocks occluding carbon dioxide are disintegrated and decom-

[a] Letts, E. A., and Blake, R. F., The carbonic anhydride of the atmosphere: Sci. Proc. Royal Dublin Society, vol. 9, new series, pt. 2, 1900, p. 159.

[b] Tilden, W. A., On the gases inclosed in crystalline rocks and minerals: The Chemical News, vol. 75, 1897, pp. 169–170.

posed in the belt of weathering this carbon dioxide escapes. Since the volume of the original and sedimentary rocks which have been broken up into fine particles or decomposed so as to allow the major portion of the gases to escape is very great, the amount of carbon dioxide given off to the atmosphere from this source must be vast.

In order to obtain any idea of the net gain to the atmosphere from carbon dioxide liberated from occlusion, much more work must be done. First, an estimate must be made as to the mass of the original igneous rocks which have been broken down, and it must be ascertained how much occluded carbon dioxide there is upon an average in these rocks in order to compute the amount of carbon dioxide liberated. In the second place it must be ascertained how much occluded carbon dioxide is in the secondary rocks. Locally the sedimentary rocks are very rich in occluded carbon dioxide in consequence of the process of silication and of the partial escape of the liberated carbon dioxide. This carbon dioxide is indirectly derived from the atmosphere. Third, a part of the enormous quantity of carbon dioxide given off by volcanoes may be that originally occluded in the centrosphere. The quantity of carbon dioxide of this origin must apparently long, if not forever, remain a matter of conjecture. The total gain of the atmosphere in carbon dioxide from occlusions is the sum of that liberated from the original igneous rocks and that derived from magma, less that held in the secondary rocks.

It has been seen that various forms of carbon are subordinate original constituents of meteorites. (See pp. 945–946.) Hence, another source of carbon dioxide may have been the oxidation of the carbon contained in meteorites and the exhalation from meteorities of carbon dioxide originally contained in them in that form. However, the additions of carbon dioxide derived from meteorites can hardly have been important since the beginning of Algonkian time. Consequently this means of restoring carbon dioxide to the atmosphere is of little consequence for the period which we are considering, that in which the sedimentary rocks were built up.

Another important source of carbon dioxide is the water ascending from the zone of anamorphism. The amount of this carbon dioxide is incalculable, but certainly it is very large. The gases included in hot springs and in deep waters rising from mines are dominantly composed

of carbon dioxide. This fact has been noted again and again since the days of Bischof. "Lecoq has calculated that of the mineral springs those of Auvergne alone give off in the same time [one year] 7,000,000,000 cubic meters of the gas, an amount rather less than one-tenth of the volume produced by the annual combustion of the coal employed throughout the whole of Europe."[a] It is to be remembered that Auvergne is but a single region, and while the amount of carbon dioxide emitted is exceptional, it is approximated in other regions where there are hot carbonated springs. The total amount of carbon dioxide emitted in the few areas where it is exceptionally abundant is probably small as compared with the quantity carried by the vastly larger amount of water of the great mass of springs of the world.

If the argument given on pages 176–177, 677–679 be correct, the carbon dioxide furnished by deep-seated springs is largely that liberated by the process of silication of carbonates, although some part of it may be derived from the carbon dioxide originally occluded in the earth.

The segregation of carbon as carbonates in the sedimentary rocks is a consequence of the reaction of carbonation, and chiefly of carbonation of the silicates. These carbonates, as already seen, are mainly concentrated in the carbonate formations, but to a considerable extent are found as accessory minerals in the shales and in the sandstones. When the rocks of the zone of katamorphism are buried so deeply as to pass into the zone of anamorphism the silication of the carbonates occurs with the liberation of the carbon dioxide. That this process has taken place almost completely in the pelites thus buried is shown by the very small percentage of carbonates in the schists, which are the metamorphosed equivalents of ancient muds. The silication of the limestones which have passed into the zone of anamorphism is in various stages, ranging from slight to complete. It is certain that this process is going on at the present time on a very great scale. Indeed, it is not impossible that the process of silication in the zone of anamorphism is taking place with a close approximation to the speed of the process of carbonation in the belt of weathering.

In so far as the process of silication with decarbonation is taking place in the deep-seated zone, and the liberated carbon dioxide is carried by the ground water to the atmosphere or to the hydrosphere, the depletion of the

[a] Letts and Blake, cit., p. 159.

atmosphere and the hydrosphere in carbon dioxide by carbonation is compensated.

In the early eras of the deposition of the sedimentary rocks, before carbonates existed in important quantity, it is certain that carbonation far outclassed silication; for before the latter process became important, carbonates were necessarily formed in large amounts and buried to a considerable depth. The existence of the vast amounts of carbonates in the sediments is evidence that carbonation has greatly exceeded silication.

The further carbonation advances the more abundant become the carbonate formations, many of which in due time are buried to a great depth, and thus the more important becomes silication. And finally, in the natural course of events, the two processes will approach each other in quantitative value. The carbono-silicic cycle will approach a balance. But that silication is now keeping pace with carbonation is not asserted. Only conjecture can be offered on that point. While silication of carbonates may not yet equal carbonation in amount, it is believed that the former process directly or indirectly returns to the atmosphere a large percentage of the carbon dioxide abstracted from it by carbonation.

Another obvious source of carbon dioxide for the atmosphere is the oxidation of the carbonaceous materials of the earth. It has been pointed out that nearly as fast as organisms are produced they are decomposed. In so far as both processes occur there is neither loss nor gain of carbon dioxide to the atmosphere. But continuously during a large part of geological time a residual portion of the organic material has not decomposed, and thus the carbonaceous deposits have been built up, abstracting carbon dioxide from the atmosphere. (See pp. 949, 966–967.) In so far as the processes of the belt of katamorphism result in the storing of carbon in the various hydrocarbons within the earth there is continuous depletion of the carbon dioxide of the atmosphere, and during much of geological time this has been a steady, cumulative process. But recently man has begun artificially to oxidize these carbonaceous materials. Until the last half of the nineteenth century this was unimportant, but in recent years the oxidation of carbonaceous material once buried within the earth has been carried on on an enormous scale. As calculated on page 464, the combustion of 1,000,000,000 metric tons of coal turns into the atmosphere 2,933,333,000 metric tons of carbon dioxide. Thus, at this annual rate of combustion of

coal, in 812 years the amount of carbon dioxide added by this process would be equal to the total carbon dioxide of the atmosphere.

Possibly carbon dioxide may be steadily gathered to the earth from the interplanetary or interstellar spaces by the force of gravity. According to Hunt, this idea was first suggested by Sir William Grove in 1843.[a] This source of carbon dioxide Hunt regards as the chief one. The possibility of segregation of carbon dioxide from the stellar spaces has been recently brought forward again by Chamberlin.[b]

If we write an equation representing the amount of carbon dioxide in the sedimentary rocks we have the following:

$$(2.64+.81\times 44/12)\times .65+(3.03\times .30)+(38.58\times .05)=6.4585.$$

In the above equation 2.64 is the CO_2 in shales and 0.81 is the carbon contained as carbonaceous material in shales, which must be multiplied by 44/12 in order to find the equivalent amount of CO_2. The above equation does not take into account coal and other especially carbonaceous deposits, which would increase the quantity. Even omitting the coal deposits, the average amount of carbon in the sedimentary rocks is 8 times greater than Clarke's estimate of the amount of carbon dioxide in the original igneous rocks, 0.81 per cent. As in the case of sulphur, it is not necessary to suppose that these two amounts should balance, for there may have been originally a large amount of carbon dioxide in the atmosphere and hydrosphere not derived from the crystallized rocks. Also, as has been pointed out, it is little short of certain that the carbon originally in magma, either as carbon, hydrocarbons, or carbon dioxide, largely escapes as carbon dioxide at the time of the crystallization of the rocks. At this time of escape the hydrocarbons and carbon are largely oxidized to CO_2. However, the above equation shows it to be certain that the original crystallized igneous rocks do not constitute the sole, or even the chief, source of the carbon which has taken such an important part in the economy of the earth.

In summary it appears that the carbon of the lithosphere was originally widely dispersed in small quantities. The operations of metamorphism concentrate carbon in the carbonates and carbonaceous deposits, and to a

[a] Hunt, T. Sterry, The geological relations of the atmosphere: Rept. Brit. Assn. Adv. Sci., 1878, p. 544.

[b] Chamberlin, T. C., A group of hypotheses bearing on climatic changes: Jour. Geol., vol. 5, 1897, pp. 653–683.

less extent in the carbonaceous shales. The direct source of the carbon for this concentration is the atmosphere, which has been continuously replenished in various ways.

The certain original sources of carbon dioxide for the replenishment of the atmosphere were the magmas and meteorites. Silication, the oxidation of organic material, and the ocean return to the atmosphere carbon dioxide which has been taken from it. But all of the above supplies of carbon dioxide are available to replenish the atmosphere. Concluding, the chief processes which abstract carbon dioxide from the atmosphere are those of carbonation and the building up of carbonaceous deposits. All of the replenishing processes, including the reversing processes of silication and the oxidation of buried carbon compounds, have been barely able to keep a minute portion of carbon dioxide in the atmosphere—0.030 per cent by volume, or 0.045 per cent by weight. It is probable, however, that the work of man, especially during the last half century, has returned a great volume of carbon dioxide to the atmosphere by the artificial oxidation of carbonaceous material, and thus has reversed the average of the processes of nature, which plainly appear to have caused depletion of the carbon dioxide in the atmosphere. In consequence, at the present time the amount of carbon dioxide in the atmosphere may be increasing rather than decreasing.

TITANIUM.

According to Clarke's estimate of 1891 titanium comprises 0.30 per cent of the original rocks, the lithosphere, and the atmosphere together. All of the titanium is in the original rocks, of which it composes 0.33 per cent. In 1900 Clarke increased his estimate of titanium in the original rocks to 0.41 per cent, thus giving it ninth place in the scale of abundance next to potassium. In passing from sodium to titanium we go from the elements which may be called abundant to those which are subordinate. Reckoned as an oxide (TiO_2) Clarke's estimate of the amount in the original rocks for 1891 is 0.55 per cent and for 1900 is 0.60 per cent.

In the original rocks titanium occurs both as an oxide and as a titanite. As an oxide it is found in ilmenite and in the rutile group. As a titanite it is found in titanite and perovskite. The amount of these minerals in the rocks is not usually large, but they are very widespread. The

original magnetite of many rocks is strongly titaniferous, and because of its abundance may be the chief home of titanium.

Titanium forms 0.65 per cent of 78 shales; 0.33 per cent of 624 sandstones, and 0.07 per cent of 843 limestones. It thus appears that as compared with the original rocks the amount of titanium is somewhat increased in the shales, is reduced to a little more than one-half in the sandstones, and is less than one-eighth in the limestones. If one were to estimate the amount of titanium in the original igneous rocks by the amount in the sedimentary rocks we would have the following equation:

$$.65\times.65+.33\times.30+.07\times.05=.525.$$

This accords very well with the actual amount as estimated by analyses in the original igneous rocks, 0.55 to 0.60 per cent. The minerals produced by metamorphism are the same as those of the original rocks. The details of the transformations with reference to the different zones and belts of metamorphism have not been worked out. Titanium minerals have been especially observed in the metamorphosed pelites and psephites, and to this observation the analyses above given correspond.

PHOSPHORUS.

According to Clarke's estimate of 1891 phosphorus forms 0.09 per cent of the outer 10 miles of the crust of the earth, including the original rocks, hydrosphere, and atmosphere. All of it is in the lithosphere, of which it composes 0.10 per cent. In his estimate of 1900 Clarke reduces this amount to 0.09 per cent.

Phosphorus is thus twelfth in the scale of abundance, ranking next to carbon, an element of vastly greater importance. Reckoned as an oxide Clarke's estimates of 1891 and 1900 are both 0.22 per cent.[a] This gives phosphorus oxide eleventh place in the table of oxides. In the original rocks phosphorus is known to occur only in the mineral apatite, of which it composes 18.47 per cent. This mineral, while usually subordinate in amount, is very widespread. In the meteorites phosphorus is found in schreibersite ($FeNiCoI_3P$). (See p. 946.) The amount of P_2O_5 in 78 shales is 0.17 per cent; in 624 sandstones 0.07 per cent; in 345 limestones not used for building purposes is 0.04 per cent, while in 498 limestones used for building purposes it is 0.42 per cent.[b]

[a] Clarke, cit., Bull. 78, p. 39; Bull. 168, p. 15.

[b] Clarke, cit., Bull. 168, p. 14.

The amount of P_2O_5 in the limestones used for building purposes rather than the average of all limestones is taken, as probably more nearly representing the average amount of phosphorus in these rocks, since it is well known that in the belt of weathering the phosphorus is leached out.

Therefore it appears that the amount of P_2O_5 in the shales is about three-fourths of that present in the original rocks; in the sandstones is about one-third; and in the limestones is nearly doubled. If one multiplies the amount of P_2O_5 in each of the sediments by their estimated quantities, and adds them together, we have the following equation:

$$.17\times.65+.07\times.30+.42\times.05=.1525.$$

This shows a deficiency of about one-third of P_2O_5, as compared with the original rocks. A portion of this deficiency is undoubtedly accounted for by the phosphate rock deposits, such as those of South Carolina, Florida, and Tennessee, and by the guano deposits. These represent the economic products of segregating processes which have increased the proportional amount of phosphorus many fold.

All agree that the first stage of the segregation of phosphates in the sedimentary rocks is accomplished through the agency of animals. For the guanos this first concentration is made by sea birds. For the more extensive phosphate deposits the first concentration of phosphorus was by invertebrate animals, such as brachiopods and crustaceans, and by vertebrates, such as sharks and saurians. Very commonly this first concentration is in limestones. The further concentration of the phosphorus of guanos and that of phosphatic limestones and other rocks is by underground water. The circulations producing the concentration and the forms of the resultant deposits are multifarious, but the general principle applicable to most cases appears to be that the phosphates are dissolved by descending waters in the belt of weathering and thrown down on reaching the belt of cementation.[a] Usually the latter reaction takes place in the upper part of the belt of cementation, so that the phosphates are segregated at or just below the level of ground water. The precipitation of the phosphates is especially

[a] Penrose, R. A. F., jr., Nature and origin of deposits of phosphate of lime: Bull. U. S. Geol. Survey No. 46, 1888, pp. 1–143. Dall, W. H., and Harris, G. D., Correlation papers—Neocene; Phosphatic deposits of Florida: Bull. U. S. Geol. Survey No. 84, 1892, pp. 134–140. Eldridge, Geo. H., A preliminary sketch of the phosphates of Florida: Trans. Am. Inst. Min. Eng., vol. 21, 1893, pp. 196–231. Hayes, C. W., The Tennessee phosphates: Seventeenth Ann. Rept. U. S. Geol. Survey, 1895–96, pt. 2, 1896, pp. 513–550.

likely to occur in limestone. Eldridge suggests that under such circumstances the precipitation is brought about "by the simple interchange of bases between the phosphate and carbonate of lime thus brought together, or by the lowering of the solvent power of the waters through loss of carbonic acid. The latter would happen whenever the acid was required for the solution of additional carbonate of lime, or when, through aeration, it should escape from the water. The zone of phosphate deposition was apparently one of double concentration, resulting from the removal of the soluble carbonate thus raising the percentage of the less soluble phosphate, and from the acquirement of additional phosphates of lime from the overlying portions of the deposit."[a]

The precipitated phosphate is likely to be deposited in nodules. This material is more resistant than the containing limestone. Through erosion by streams or ocean there may be a further concentration of the phosphates due to the greater resistance of the phosphate to both solution and mechanical wear as compared with limestone.

The bedded Devonian phosphates of Tennessee are in part, according to Hayes, an important exception to the above, the phosphatic material of the beds being regarded by him as largely concentrated when originally laid down.[b]

Whether or not the sedimentary rocks rich in phosphates not considered in the analyses of shales, sandstones, and limestones are sufficient to account for the deficiency in these rocks in phosphorus is undetermined. In this connection it should be remembered that the vein phosphates of Canada, Norway, and similar phosphatic rocks, in which a large amount of phosphorus is concentrated probably in consequence of original igneous or pegmatitic processes, are also excluded from the original rocks, and in so far as these deposits occur they offset the concentrations of the sedimentary phosphatic deposits.

The redistribution of phosphorus by the ordinary metamorphic processes has as yet been little studied. In the iron-ore deposits in which phosphorus is a very important economic compound such studies have been begun, but as yet no general conclusions have been reached.

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[a] Eldridge, Geo. H., cit., p. 216.

[b] Hayes, C. W., and Ulrich, E. O., Description of the Columbia [Tennessee] quadrangle: Geologic Atlas U. S., folio 95, U. S. Geol. Survey, 1903, pp. 4–6.

CHLORINE.

According to Clarke's estimate of 1891 chlorine, including bromine, forms 0.15 per cent of the original rocks, the hydrosphere, and the atmosphere. Of the ocean it composes 2.07 per cent. His estimate for the original rocks in 1891 and 1900 is the same, 0.01 per cent.

As to the source of chlorine the only minerals of the original igneous rocks in which it is found are apatite, sodalite, and the marialite molecule of the wernerites. Chlor-apatite and marialite are very unimportant original minerals, and therefore the chief mineral in which it is found is sodalite, of which it constitutes 7.3 per cent.[a]

It has already been explained (pp. 789–790) that chlorine is emitted from volcanoes as hydrochloric acid and to a less extent as chlorine. It has been further noted that a part of this chlorine may possibly have been derived from sea water; but there is reason to suppose that much of it is that of the original magmas. So far as this is true we have an original source for chlorine. And when it is considered that at periods of regional volcanism the amount of chlorine which probably issued from volcanoes was vastly greater than at the present time of local volcanism, it follows as a possibility that volcanism is the most important source of that element.

In the meteorites chlorine occurs in lawrencite ($FeCl_2$). Lawrencite is a volatile and readily decomposable mineral. If at the time the earth stuff segregated chlorine was contributed as lawrencite, it is certain that the action of water in the magmas upon this compound would produce hydrochloric acid; this suggests a source of a part of the hydrochloric acid of volcanoes.

In the secondary rocks the amount of chlorine is very small. In the mechanical sediments it is so small that it can not be estimated. It is not mentioned in the analyses of the shales, and only a trace is reported in the sandstones. In 843 limestones chlorine composes 0.01 per cent. The sea water which was originally between the pores of the mechanical sediments must have contained considerable chlorine. The absence of chlorine from the mechanical sediments shows how thoroughly the sea water has been squeezed or leached out in the transformations of the rocks from their original forms to shales, sandstones, etc. The presence of

[a] Dana, E. S., A system of mineralogy, Wiley & Sons, New York, 6th ed., 1892, p. 429.

an amount of chlorine in the limestones somewhat greater than the average for the original rocks is not easy to understand. The explanation may lie in the fact that limestones are the home of the phosphates and that the phosphate apatite is a chlorine-bearing mineral.

A large part of the chlorine which was present in the original igneous rocks and which has escaped into the atmosphere through volcanoes has passed into the hydrosphere. Under ordinary conditions, after the chlorine is once taken into solution apparently very little of it is again redeposited. It continues in the circulating waters until it reaches the sea, in which it appears to have been segregating during geological time. Of all the elements of the salts of the sea it is by far the most abundant. According to Dittmar's estimates it composes 55.292 per cent of the total salts, or more than half of all the compounds held in solution in the sea. This would amount to 25,557,000,000,000,000 metric tons.

While a large part of the chlorine which has been subjected to metamorphic processes has been carried to the sea, at places where there are inclosed basins, as for instance the Great Basin, the Dead Sea, etc., chloride deposits have been built up. Locally these are of considerable magnitude. Moreover, during geological ages chloride deposits, mainly of sodium, have accumulated in abundance, so that considerable beds containing variable percentages of chlorine have been buried below later sediments. Such material furnishes the rock salt of the salt mines, for instance, of Poland, and the brines of many salt-producing districts, such as those of New York and Michigan.

As yet it is entirely impracticable to estimate the amount of chlorine which is locked up in the rocks as sodium chloride. It has been the common impression that the major portion of the sodium chloride is in the sea rather than in such deposits. It is subsequently suggested that this impression may be erroneous (see pp. 997–998), and that the great amount of segregated sodium is in the salt deposits rather than in the sea. If this be true for that element, it would also be true for chlorine.

The chlorine concentrated with sodium in the salt deposits and the sea is the great economic product resulting from the segregation of this element in large proportions from material originally very sparsely disseminated. The great importance of sodium-chloride to man and to animal life in general is so well known that it need not be emphasized.

NITROGEN.

Nitrogen forms 0.02 per cent of the outer 10 miles of the crust of the earth including the lithosphere, hydrosphere, and atmosphere.[a] All but an inestimably small quantity of this is in the atmosphere, of which it composes 76.88 per cent by weight. (See p. 944.) It stands sixteenth in the scale of abundance. Nitrogen is among the gases which are occluded in meteorites; but what portion of this nitrogen is absorbed by the meteorites while passing through the atmosphere and what portion has been brought in from the interplanetary spaces is uncertain. The amount of nitrogen in the average sedimentary rocks, such as shales, sandstones, and limestones, is so small as to be inestimable.

It has been explained that in consequence of the action of bacteria and leguminous plants nitrogen is fixed in the belt of weathering, and nitrates are formed. These nitrates in arid regions are locally segregated in the belt of weathering in considerable amounts, forming the nitrate deposits. The bases with which the nitrogen is combined are almost exclusively sodium and potassium. Since the nitrates are now forming in large quantities (see pp. 452–453, 465–466) the total amount of the compounds which have been produced through geological time must have been large. But the nitrates readily break up into their original elements, and the liberated nitrogen and oxygen rejoin the atmosphere. Thus there is a continuous cycle by which nitrogen, oxygen, and carbon are united by means of the leguminous plants and bacteria; and by decomposition reduced to the original elements and carbon dioxide.

While the total quantity of nitrates is inconsiderable, as compared with the majority of the other important elements concerned in metamorphism, nitrogen is essential for the growth of plants and animals. Hence nitrogen is one of the necessary elements in the sequence of events by which carbon is abstracted from the atmosphere, passes into the plants, and thence by oxidation is concentrated so as to carry on the process of carbonation. Therefore a chief importance of nitrogen in metamorphism is as one of the aids in the chain of reactions in connection with carbon.

The nitrates in the soil and the nitrate deposits represent the economic products resulting from the abstraction of nitrogen from the air and its segregation in solids.

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[a] Clarke, cit., Bull. 78, p. 39.

HYDROGEN.

According to Clarke hydrogen composes 0.94 per cent of the outer 10 miles of the crust of the earth, including the lithosphere, hydrosphere, and atmosphere. The larger part of the hydrogen is in the hydrosphere, of which it composes 10.67 per cent. According to Clarke's estimates of 1891 and 1900 it constitutes, respectively, 0.21 and 0.17 per cent of the lithosphere.[a] The hydrogen of the atmosphere is inappreciable. It thus appears that 0.8 or more of the hydrogen is concentrated in the hydrosphere, although the volume of the lithosphere is five times as great. Hydrogen has the tenth place in the scale of abundance. Practically all of the hydrogen is combined. In so far as hydrogen enters into the processes of metamorphism it is in conjunction with oxygen as water. The source of the water is very largely conjectural. It may be supposed that hydrogen and oxygen, united as water, at the time the earth segregated, were with the other ingredients in great volume. As magma crystallized the water separated. This process has continued to the present time. By it some explain the ocean, and hold to its continuous growth in magnitude. It is possible that a considerable amount of the hydrogen for the water was originally in the free state or in the form of carbureted hydrogen. This is suggested by the fact that hydrogen and carbureted hydrogen are both occluded in meteorites. If the water of the hydrosphere was produced in any large measure by the oxidation of hydrogen an enormous quantity of hydrogen was thus consumed.

Probably the most characteristic reaction of the zone of katamorphism is that of hydration. This process, while taking place most rapidly in the belt of weathering, occurs continuously throughout the vast volume of the belt of cementation. According to Clarke[b] the combined water in the igneous and crystalline rocks liberated at 110° C. is 0.40 per cent, and above 110° C. 1.52 per cent; total, 1.92 per cent. In 78 shales the water liberated at 110° C. is 1.34, and above 110° is 3.68 per cent; total, 5.02 per cent. In 624 sandstones at 110° it is 0.29 per cent, and above 110° is 1.40 per cent; total, 1.69 per cent. In 843 limestones at 110° it is 0.26 per cent, and above 110° is 0.72 per cent; total, 0.98 per cent. (See p. 938.) It therefore appears that the amount of water in the shales is more than double and in

[a] Clarke, cit., Bull. 78, p. 39; Bull. 168, p. 15.

[b] Clarke, cit., Bull. 168, p. 14.

the sandstones and limestones is less than the average for the original rocks. The increase in the amount of combined water in hydrating the materials of the shales, 0.65 of the sediments, 438,750,000,000,000,000 metric tons, from 1.92 to 5.02 per cent, is 13,601,250,000,000,000 metric tons. The decrease in the combined water in the sandstones, 0.30 of the sediments, 202,500,000,000,000,000 cubic kilometers, from 1.92 to 1.69 per cent, is 465,750,000,000,000 metric tons. The decrease of the water in the limestones, 0.05 of the sediments, 33,750,000,000,000,000 metric tons, from 1.92 to 0.98 per cent, is 317,250,000,000,000 metric tons. The total decrease in the sandstones and limestones is 783,000,000,000,000 metric tons, which sum, subtracted from the increase in the amount of water in the shales, leaves a net increase in the water of hydration of the zone of katamorphism of 12,818,250,000,000,000 metric tons, and an equivalent loss of water to the hydrosphere.

This estimated amount is probably too small, for the following reasons:

Throughout the immense thickness of the zone of katamorphism, hydration is the rule. A very large portion of this zone is composed of igneous rocks, and the minerals of these rocks have been hydrated to a varying extent. In the plutonic rocks which have not been fractured in a complex way the process has usually not gone far, but in the volcanic rocks, and especially the porous ones, such as basalts, hydration has taken place upon a vast scale. For instance, in various parts of the world, such as in the Lake Superior region and in the Deccan, hydration has gone so far in the basic amygdaloidal lavas as in many cases to have completely destroyed the original minerals. One of the results of such alterations is the filling of the pores of the vesicular rocks with various minerals of which hydrous silicates, such as the chlorites, zeolites, etc., are especially abundant. The process of hydration of the zone of katamorphism has continued during geological time. So far as I can see there is no way to estimate the amount of water thus absorbed, but I suspect that the amount abstracted from the hydrosphere by the process is probably greater than that used in the hydration of the sedimentary rocks.

In consequence of the hydration of the original rocks of the zone of katamorphism, it is certain that the amount of combined water in the igneous and crystalline rocks analyzed in order to determine the composition of the lithosphere is greater than in the recent igneous rocks. The

analyses of the freshest modern rocks usually show less than 1 per cent of combined water. It follows that, in regarding the original rocks as containing 1.92 per cent of water, the calculated amount of water for the hydration of the sediments is too small.

In the zone of anamorphism the dehydration of the rocks which have been hydrated in the zone of katamorphism and passed into the zone of anamorphism, is not complete. Even the coarsest schists and gneisses ordinarily contain from 1.5 to 2 per cent of water. In so far as the process of dehydration of the rocks, which have passed into the zone of anamorphism is incomplete, water has been abstracted from the hydrosphere.

But even if the total of all the above could be estimated this would give no idea of the amount of water which has been added temporarily to the rocks by hydration during geological time. From the earliest time to the present hydrated sedimentary rocks formed in the zone of katamorphism have passed continuously into the zone of anamorphism, and have been steadily dehydrated. No data are available to estimate the amount of water which has been added by hydration and liberated by dehydration.

The question naturally arises as to what extent at the present time the process of dehydration is reversing that of hydration. It seems certain that hydration is taking place more rapidly than dehydration. While an estimate of the amount by which hydration exceeds dehydration would be very desirable, I see no way in which a quantitative result on this point can be even approximated.

While the amount of water abstracted from the hydrosphere by hydration is large, it does not follow that the ocean is decreasing in magnitude; for the water continuously added to the hydrosphere by the liberation of occluded water through volcanism and the crystallization of magma may more than compensate for the losses due to hydration.

ALUMINUM.

Aluminum is the most abundant of the metals of the lithosphere. Clarke's original estimate in 1891 was that aluminum constituted 7.26 per cent of the lithosphere, hydrosphere, and atmosphere, all of this being in the rocks, of which it composed 7.81 per cent. Clarke's estimate of 1900 increases the amount in the original rocks to 8.16 per cent.[a] It therefore

[a] Clarke, cit., Bull. 78, p. 39; Bull. 168, p. 15.

appears that aluminum, the most abundant of metals, is only about one-third as abundant as silicon, and only about one-sixth as abundant as oxygen. The metal takes third place among the elements. Reckoned as an oxide, in 1891 Clarke estimated the aluminum as 15.04, and in 1900 as 15.41 per cent. As an oxide it stands second only to silicon.

Aluminum has its chief source in the silicates, which occur very abundantly in the original rocks. The aluminous silicates occur also in the meteorites. By far the most important of the silicates bearing aluminum are the feldspars, which, as Clarke calculates, compose about 60 per cent of the mass of the original rocks. A large part of the remainder of the aluminum is in the pyroxenes and amphiboles, which, as Clarke estimates, compose 18 per cent of the original rocks. A smaller amount of the aluminum is in the micas, which, as Clarke calculates, compose 4 per cent of the original rocks.[a] Very subordinate amounts of alumina occur in other silicates, the more important of which are nephelite, leucite, and sodalite. Alumina occurs also in sufficient amount in corundum, gibbsite, and other oxides to deserve mention.

In 78 shales the alumina amounts to 15.47 per cent,[b] in 624 sandstones to 5.37 per cent, and in 843 limestones to 1.28 per cent. From the analyses given by Clarke it appears that as a result of the denuding and metamorphic processes alumina accumulates slightly in the shales, as compared with the amount present in the original rocks, and in the sandstones diminishes to about one-third, and in the limestones to a small fraction. According to Clarke's figures, the increase in the amount of alumina in the shales over that in the original rocks is trivial. This increase in the shales is sufficient to account for only a small part of the deficiency in the sandstones and limestones. The equation

$$15.47\times.65+5.37\times.30+1.28\times.05=11.7305$$

gives us the average of the alumina for the sediments. Therefore the analyses give a deficiency of 3.68 per cent of alumina, or nearly one-fourth, as compared with the original rocks. When it is remembered that aluminum is by far the most abundant of the metals, it will be appreciated that this deficiency is enormous.

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[a] Clarke, cit., Bull. 168, p. 16.

[b] Clarke, cit., Bull. 168, p. 17.

To some extent this deficiency is accounted for by the bauxite and gibbsite deposits, which serve as ores of aluminum. Rather extensive deposits of this kind are known in France and in the United States, in Georgia, Alabama, and Arkansas. The French deposits are ascribed "by Coquand and Augé to mineral springs or geysers, which brought the material of which they are composed to the surface and supplied it to lakes, where it was deposited along with other sediments."[a]

Hayes has discussed the Georgia-Alabama and the Arkansas deposits. The source of the Georgia-Alabama bauxite he regards as shales which underlie limestones. These shales contain pyrite.

> It is believed that surface waters carrying oxygen in solution gained access to these shales and by oxidizing the pyrites set free sulphuric acid. This, under the conditions present, decomposed the aluminous shales, forming alum and sulphate of aluminum. Ascending currents carried these salts in solution to the surface, and, coming in contact with the limestone during their upward passage, they were decomposed, forming sulphate of lime and aluminum hydroxide, together with basic sulphate of aluminum, which was subsequently changed to aluminum hydroxide on exposure to the air. The aluminum hydroxide thus produced formed a gelatinous precipitate which collected about vents of springs. It was kept in motion by the ascending water and thus formed concentric structures.[b]

The Arkansas deposits are regarded as produced by an underground circulation in a manner somewhat similar to those of Georgia and Alabama; but the source from which the alumina is derived is syenite, and the springs, instead of issuing on the land, issue under water, and thus the deposits are somewhat more widely distributed. Many of the springs issue directly above the syenite, and therefore the bauxite deposits overlie the undulating syenite surface. Other springs issue through the adjacent Tertiary sediments, which in such cases are overlain by the bauxite deposits.[c]

Bauxite deposits of character somewhat similar to those of France and the United States are known in other parts of the world, but probably the total amount of alumina segregated in all the known bauxite deposits is but an insignificant fraction of the deficiency above calculated for the ordinary sediments.

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[a] Hayes, C. W., Bauxite: Sixteenth Ann. Rept. U. S. Geol. Survey, pt. 3, 1895, p. 548.

[b] Hayes, C. W., The Arkansas bauxite deposits: Twenty-first Ann. Rept. U. S. Geol. Survey, pt. 3, 1900, p. 461.

[c] Hayes, cit., pp. 464–466.

It therefore appears to me that we must look somewhere else to explain the greater part of the discrepancy. It is certain that when the shales (the sedimentary rocks into which the aluminous minerals mainly pass) are metamorphosed in the zone of anamorphism, the secondary minerals show an excess of alumina. All of the chief original aluminous minerals, viz, feldspar, pyroxene, amphibole, and mica, may be reproduced; but there also develop other aluminous minerals which are not known in the original rocks. Of these, garnets, staurolite, and the aluminum-silicate minerals—andalusite, sillimanite, and cyanite—are by far of the greatest consequence. The latter minerals are especially characteristic of rocks of the approximate composition of the pelites metamorphosed in the zone of anamorphism. They clearly mark an excess of aluminum and furnish almost conclusive evidence of the segregation to a considerable extent of the aluminum in the pelites beyond the amount which is present in the original rocks.

This argument has such weight that I believe more careful analyses of shales with reference to their mass and chemical composition will show that the alumina ought to be considerably higher than in the analyses given. It has already been noted (p. 962) that correlative with the deficiency of alumina there is apparent excess of silica in the shales, and the deficiencies and excesses are remarkably accordant. It has just been seen that the apparent deficiency in alumina is 3.68 per cent. A small fraction of a per cent can be accounted for by the bauxite deposits. The excess of silica as shown by the calculations (p. 961) is 3.247 per cent. Consequently the two nearly balance. I venture to predict that when more satisfactory average analyses are available the shales will be found to contain several per cent more alumina and several per cent less silica than is given in the average analyses of shales on page 938.

IRON.

According to Clarke's estimate of 1891 iron composes 5.08 per cent of the outer 10 miles (16.1 kilometers) of the crust of the earth, including the lithosphere, hydrosphere, and atmosphere, and 5.46 per cent of the original rocks alone. In his estimate of 1900 Clarke estimates that the iron forms only 4.64 per cent of the original rocks.[a] This gives iron fourth place among the elements, it being surpassed only by oxygen, silicon, and aluminum. Reckoned as an oxide, according to Clarke's estimate of 1891,

[a] Clarke, cit., Bull. 78, p. 39; Bull. 168, p. 15.

the amount of ferric oxide is 3.94 per cent and of ferrous oxide is 3.48 per cent, and in his estimate of 1900 the ferric oxide is 2.63 per cent and the ferrous oxide 3.52 per cent. Reckoned as an oxide, iron thus has the third place in abundance, being surpassed only by silica and alumina.

Iron occurs as an original constituent of the igneous rocks in perhaps more numerous forms than any other element. It is found as a sulphide as pyrite, pyrrhotite, etc.; and as an oxide as hematite, magnetite, and ilmenite. It occurs in many silicates. Of these, the pyroxenes and amphiboles, the olivines, and the micas are the more important. In the meteorites iron is the most abundant constituent, occurring alloyed with nickel and cobalt, and in sulphides, oxides, silicates, etc.

In 78 shales the ferric oxide is 4.03 per cent of the rock, the ferrous oxide 2.46 per cent; in 624 sandstones the ferric oxide is 1.24 per cent, and the ferrous oxide 0.57 per cent; in 843 limestones the ferric oxide is 0.66 per cent, the ferrous oxide being undetermined.[a]

The 4.03 per cent of ferric oxide and the 2.46 per cent of ferrous oxide in the shales is equivalent to 4.73 per cent metallic iron. The 1.24 per cent of ferric oxide and the 0.57 per cent of ferrous oxide in the sandstones is equivalent to 1.31 per cent metallic iron. The 0.66 per cent of ferric oxide in the limestones is equivalent to 0.462 per cent metallic iron. It thus appears that there is a slight increase, less than 0.1 per cent, in the amount of iron in the shales as compared with the original rocks. There is great depletion of iron in the sandstones—which contain between one-third and one-fourth of the amount in the original rocks. The depletion of the iron in the limestones is very great—there being about one-tenth the amount in the original rocks. The slight increase in the shales is by no means sufficient to account for the depletion of the sandstones and limestones. If we multiply the percentage of iron present in the different kinds of sediments by the estimated quantity of those sediments, and add the three together, we have the following equation:

$$4.73 \times .65 + 1.31 \times .30 + .462 \times .05 = 3.491 \text{ per cent.}$$

Since the amount of iron present in the original rocks is 4.64 per cent, this shows a deficiency of 1.149 per cent for the entire mass of sediments. This difference seems small, but it amounts to 7,155,750,000,000,000

[a] Clarke, cit., Bull. 168, pp. 16, 17.

metric tons of metallic iron. The question naturally arises, What has become of this enormous amount of iron? The processes of metamorphism have segregated from 30 to 70 per cent of iron in the various iron-bearing formations and in the iron-ore deposits. (See pp. 842–846, 1193–1198.)

While the iron-ore deposits themselves contain much the larger percentage of iron, the main mass of the segregated iron is in the iron-bearing formations rather than in the iron ores. Indeed, the amount in the iron ores is probably insignificant as compared with the amount in the iron-bearing formation. For instance, in the Mesabi district of Minnesota, where the iron-ore deposits are larger than in any other region, Doctor Leith has calculated that in the part of the iron-bearing formation which is exposed at the surface, including no part which passes below the overlying slate, the amount of disseminated iron is probably one hundred times as great as that contained in the ore deposits. And the amount of this formation below the slates, in which there are no known ore deposits, is certainly many times, probably hundreds of times, that exposed. This calculation in reference to the Mesabi range shows how trivial is the amount of iron in the ore deposits as compared with the more widely distributed lower-grade products of the iron-bearing formations Such formations are illustrated by the great pre-Cambrian iron-bearing formations of various parts of the world, such as those occurring in the Lake Superior region; by the very extensive iron-bearing member and the ores of the Clinton horizon of the Silurian; by the great iron-bearing horizons of the Carboniferous, and by the bog deposits of the Pleistocene. It is believed that if the iron-bearing formations and the iron ores associated with them were represented in the above equation in proportion to their mass and percentage of iron, the excess of iron in them beyond that of the original rocks would be nearly or quite sufficient to account for the great deficit of iron shown by the ordinary sediments. The segregation of the iron in the iron-bearing formations and the ores is treated on pages 102–130, 823–846, 1193–1198.

In the zone of katamorphism many minerals are produced by the alteration of the original iron-bearing minerals. Of these the hydrated oxides of iron, especially limonite, and the silicates, such as the chlorites and the epidotes, are important. Where the rocks pass into the deep-seated zone any of the minerals in which the iron originally occurred may be reproduced.

Other iron-bearing minerals also are formed. Among them garnet and staurolite are important; but various other heavy iron-bearing silicates develop, among which may be mentioned ilmenite, humite, clinohumite, ottrelite, and chloritoid.

MANGANESE.

According to Clarke's estimate of 1891 manganese forms 0.07 per cent of the outer 10 miles of the crust of the earth, including the lithosphere, hydrosphere, and atmosphere. In the lithosphere alone the amount estimated is 0.08 per cent. In his estimate of 1900 he reduces this amount to 0.07 per cent.[a] By this estimate manganese is thirteenth in the scale of abundance. If these amounts of 0.08 and 0.07 per cent were reckoned as MnO_2 they would be respectively 0.1265 and 0.1107 per cent.

Very small percentages of manganese are reported in the following silicates: låvenite, arfvedsonite, spessartite, piedmontite, and astrophyllite. The amount in no case is large enough to make the element an essential one. Manganese is reported among the subordinate constituents of the meteorites. A trace of it is reported in the shales and sandstones, and in 843 limestones manganese oxide composes 0.04 per cent of the rock. Since the mass of the limestones is so small as compared with the shales and sandstones, manganese in the limestones is trivial compared with that which is present in the original rocks. The probable explanation of the deficiency of manganese in the common secondary rocks is that the manganese is segregated in manganese ore deposits precisely as the iron, the reactions for segregation being analogous throughout. (See pp. 1198–1199.) Thus the manganese reported in the sedimentary rocks is found in limestones—that is, in carbonate rocks. Iron is, in a similar manner, to a large extent segregated in connection with carbonate deposits.

The relative masses of the segregated manganese ore and iron ore are interesting, since these two compounds go through analogous transformations, producing ore bodies under similar conditions, and in very numerous cases being associated in the same ore deposits. But subject to the law of mass action the abundant element iron produces ore deposits of enormously greater size than does the rarer element manganese. The amounts of iron and manganese in the original rocks are 4.64 and 0.07 per cent respectively. Thus if the two elements were segregated in the

[a] Clarke, cit., Bull. 78, p. 39; Bull. 168, p. 15.

same proportion by the processes of metamorphism the iron-ore deposits should be 66.3 times as great in magnitude as the manganese deposits, and this ratio is certainly approximated by the facts. There can be no better illustration of the importance of the chemical law of mass action in geological processes.

CALCIUM.

According to Clarke's estimate of 1891 calcium composes 3.51 per cent of the outer 10 miles of the crust of the earth, including the original rocks, hydrosphere, and atmosphere; of the original rocks alone 3.77 per cent, and of the ocean alone 0.05 per cent. According to his estimate of 1900 the amount of calcium in the original rocks is 3.50 per cent.[a] Calcium is fifth in abundance among the elements. Reckoned as an oxide Clarke's estimate of the amount in the original rocks was 5.29 per cent in 1891, and 4.90 per cent in 1900. This gives lime fourth place in the table of oxides.

Calcium is an abundant constituent of many of the minerals of the original rocks. It occurs in all of the feldspars except the acid end of the series. It is an essential constituent of nearly all of the pyroxenes and amphiboles, being, however, more abundant in the former than in the latter. For instance in diopside the ratio between the calcium and magnesium is 1 : 1, whereas in tremolite the ratio is 1 : 3. It is an essential constituent of the scapolites, meionite and wernerite, which, however, do not form an especially important group of minerals in the igneous rocks. While calcium occurs in fewer minerals than magnesium and is less abundant than magnesium in the pyroxenes and amphiboles the fact that calcium is an essential constituent of so many feldspars which, according to Clarke's estimate, compose 60 per cent of the minerals of the original rocks, makes calcium a more abundant element than magnesium. In the meteorites calcium occurs abundantly in the feldspars and pyroxenes, and as calcium sulphide in the mineral oldhamite.

In 78 shales the calcium oxide amounts to 3.12 per cent of the rock;[b] in 624 sandstones to 3.29 per cent, and in 843 limestones to 41.60 per cent. (See p. 938.) These numbers show that the amount of calcium oxide, as compared with the original rocks, is reduced by more than one-third in the shales and about one-third in the sandstones, and is increased more than

[a] Clarke, cit., Bull. 78, p. 39; Bull. 168, p. 15. [b] Clarke, cit., Bull. 168, pp. 16–17.

eightfold in the limestones. It therefore appears that the very considerable deficiency of calcium in the abundant shales and sandstones is to be accounted for by the great concentration of calcium in the limestones. On the hypothesis that the sum of the deficiencies should equal the excess in the limestones, we have another case by which we may test the correctness of the estimates of the relative quantities of the sediments. For if the above supposition be true, the percentage of CaO in each of the kinds of sediments, multiplied by the mass of the sediments, should, added together, equal the percentage in the original rocks. Putting this in the form of an equation we have:

$$3.12\times.65+3.29\times.30+41.60\times.05=5.095.$$

The sum, 5.095 per cent, is about halfway between Clarke's estimate of 1891 of the amount of CaO in the original rocks and his estimate of 1900, being slightly less than the former and slightly greater than the latter. Therefore, so far as the criterion of analyses is applicable, the determinations of calcium seem to furnish a confirmation of the estimates of the relative masses of the shales, sandstones, and limestones.

In the above computation the amount of CaO in solution in the ocean is not considered. According to Dittmar's estimates this amount is 553,000,000,000,000 metric tons of calcium, which would correspond to 774,200,000,000,000 metric tons of CaO. The total amount in the sediments on the basis of the above analyses and estimates of relative volumes would be 34,391,250,000,000,000 metric tons. Therefore the amount in the ocean is 2.25 per cent of the estimated amount in the sediments. While the CaO in the ocean is to be regarded as derived from the destruction of the original rocks, this amount is so small as to be negligible in comparing the amount of CaO in the original and the secondary rocks.

The segregation of the calcium, with the greater segregation of carbon, in the limestones, is one of the most interesting and important results of chemical, physical, and organic processes. (See pp. 964–966). It has been pointed out that the process of carbonation in the zone of katamorphism is made effective by the concentration of carbon dioxide by plants in the belt of weathering. The carbonates produced are largely transported to the sea. In the sea the carbonates are thrown down by animals, and thus the lime-

stones are formed. While much of the $CaCO_3$ produced by carbonation is transported to the sea, a considerable part of it is transported to the belt of cementation, and enough of this is precipitated to make $CaCO_3$ a cementing agent second in importance to silica. (See pp. 624–625.) A very subordinate part of the $CaCO_3$ in the belt of cementation enters into combination with silica, forming the zeolites and epidotes.

From the foregoing it appears that the calcium in the secondary minerals of the zone of katamorphism is largely in the form of carbonate, often not a simple carbonate, but a calcium-magnesium carbonate. In this zone also are found other secondary calcium-bearing minerals, such as the zeolites and epidotes.

When the rocks containing these secondary calcium-bearing minerals pass into the zone of anamorphism, the minerals are decomposed, the carbonates by silication and the zeolites and epidotes by dehydration. In the nearly pure calcium-magnesium carbonate rocks the silicates which form most plentifully are wollastonite, diopside, tremolite, and actinolite, Naturally, where the limestones are nearly pure calcium carbonate, by silication the pure calcium silicate, wollastonite, forms. If magnesium is not very abundant, there is likely to be developed the pyroxene, diopside, in which the calcium-magnesium ratio is 1:1. Where the carbonate rocks are strongly magnesian, tremolite forms; and where they also bear iron, actinolite develops. In the rocks in which there is a considerable number of bases, such as the impure limestones, the shales, and the sandstones, other silicates form. Any of the calcium-bearing silicates occurring in the original rocks may be reproduced, and part of the calcium usually passes into heavy minerals not commonly found in the original rocks, such as garnets, melilite, the scapolites, etc.

MAGNESIUM.

According to Clarke's estimate of 1891, magnesium forms 2.50 per cent of the outer 10 miles (16.1 kilometers) of the crust of the earth, including the original rocks, the ocean, and the atmosphere. Of the ocean it comprises 0.14 per cent, and of the original rocks 2.68 per cent. In his estimate of 1900, Clarke reduces the amount for the original rocks to 2.62 per cent.[a] Magnesium thus stands seventh in the scale of abundance. It is about five-sevenths as abundant as calcium, the element with which it is

[a] Clarke, cit., Bull. 78, p. 39; Bull. 168, p. 15.

most intimately associated and most closely allied. Reckoned as an oxide, Clarke's estimate of 1891 is 4.49 per cent, and of 1900 is 4.36 per cent. This gives magnesia fifth place among the oxides. Magnesium occurs as a constituent of the original igneous rocks in a number of minerals. Of these, the pyroxenes, amphiboles, micas, and olivines are the more important. It is only rarely present in any considerable proportion in the feldspars, the most abundant group of minerals. Thus, while occurring in more minerals than calcium, it is not so abundant as calcium, because of the great rôle of the feldspars.[a] In the secondary rocks magnesia composes 2.45 per cent of 78 shales, 0.85 per cent of 624 sandstones, and 6.20 per cent of 843 limestones. It thus appears that as compared with the original rocks the amount of magnesia in the shales is reduced to about three-fifths, in the sandstones to about one-fifth, and in the limestones is increased by more than one-third. The sum of the products of the percentage of each class of sediments by their proportional amounts gives the average percentage of magnesia in the sediments, thus:

$$2.45\times.65+.85\times.30+6.20\times.05=2.1575.$$

Subtracting this 2.1575 from 4.36, the amount in the original rocks, we have a deficiency of 2.2025 per cent. The total amount of sediments multiplied by this latter percentage gives 14,866,875,000,000,000 metric tons.

The question now arises as to the explanation of this apparent vast deficiency of magnesia in the sedimentary rocks. The question is not easily answered. Possibly some part of the calculated deficiency is only apparent. Probably the composite analyses of 345 limestones, taken at random, in which the magnesia is 7.90 (see p. 938) is nearer the average for the limestones than this amount averaged with the quantity of magnesia, 4.49 in the building stones (see p. 938), since it is well known that the magnesian limestones are likely to be porous and brecciated, and therefore not so suitable for building purposes. If the average amount of magnesia in the limestone were taken as 7.90 instead of 6.20, as given in the above equation, we have:

$$7.90\times.05-6.20\times.05=.085.$$

But 0.085 per cent is only about one twenty-sixth of the calculated deficiency, and therefore we must look somewhere else for the explanation

[a] Clarke, cit., Bull. 168, p. 16.

of the major part of it. The natural direction to which we first turn to account for the deficiency is the ocean. According to Dittmar's estimates the amount of magnesium in the ocean is 1,743,000,000,000,000 metric tons, which corresponds to 2,887,800,000,000,000 metric tons of magnesia. It is at once seen that the total amount in the ocean is vast, the magnesia being between three and four times as abundant as lime. But this enormous amount accounts for only 19.45 per cent of the deficiency.

Another large portion of the deficiency is probably accounted for by magnesium in classes of the sedimentary rocks not considered—that is, the saline deposits. In all salt deposits magnesium salts are important impurities. In the water of Great Salt Lake the magnesium varies from 0.3 to 2.6 per cent of the total solids in solution;[a] in the water of the Dead Sea it is given as 14.41 per cent of the total solids.[b] In the salt deposits of New York and Michigan the magnesium in the brines varies from .034 to .454 per cent.[c] In the rock salts of Louisiana the magnesium varies from 0.003 to 0.06 per cent.[d] These figures may be taken as representative of ordinary salt deposits, but in certain exceptional salt deposits, as those of Stassfurt, the magnesium salts are much more abundant. In such deposits a great portion of the magnesium salts with the accompanying potassium salts is likely to be found in a more or less distinct bed above the rock salts. As illustrating the abundance of these compounds Precht states that at Stassfurt, from 1876 to 1880, there were mined 699,136 metric tons of carnallite ($KMgCl_3.6H_2O$), kieserite ($MgSO_4+H_2O$), and kainite ($MgSO_4.KCl+3H_2O$) and only 96,856 tons of rock salt. A considerable amount of magnesium occurs also, in accompanying polyhalite.[e] It is plain that the total quantity of the magnesium in saline deposits is great, but what portion of the deficiency is thus accounted for can not be stated until very careful studies have been made of the volumes and compositions of the salt deposits of the world.

It is believed that the explanation of a larger part of the deficiency is to be found in the concentration of magnesia in the zone of katamorphism in consequence of the alterations of that belt, the magnesia as is explained

[a] Gilbert, G. K., Lake Bonneville: Mon. U. S. Geol. Survey, vol. 1, 1890, p. 253.
[b] Encyclopedia Britannica, 9th ed., 1877.
[c] Tenth Census, vol. 2, p. 1017.
[d] Mineral Resources, 1883–84, p. 841.
[e] Precht, H., Die Salz-Industrie von Stassfurt und Umgegend, 1889, p. 12.

below, being much more largely retained in the belt of weathering and in the belt of cementation than is calcium. But as yet no data are available to enable us to make any statement as to the quantitative importance of this concentration.

To what extent the magnesium in the ocean, in the saline deposits, and segregated in the zone of katamorphism will explain the deficiency in the ordinary sedimentary rocks can not be stated. This can be determined only after a careful quantitative estimate has been made of these various supplies of magnesium. The redistribution of magnesium by metamorphism, while in many respects analogous to that of calcium, is in many respects also different. It has been seen that by the process of carbonation of the silicates by far the larger part of the calcium is released from silica and changed to carbonates. The major part of the calcium carbonate and other carbonates, such as sodium carbonate, find their way to the sea in solution. While the process of carbonation also changes a considerable portion of the magnesium of the silicates to magnesium carbonate, a very large part remains in the silicates. The olivines change to serpentine. The nonaluminous pyroxenes and amphiboles alter to talc on an extensive scale. The aluminous pyroxenes and amphiboles pass into chlorite, a magnesium aluminous silicate. The pyroxenes extensively change to amphibole, and this involves a partial substitution of magnesium for calcium, or else a subtraction of calcium and partial carbonation, or both. Thus, the magnesium is concentrated in the zone of katamorphism, and especially in the belt of weathering. But this concentration is largely due to the abstraction of other elements rather than the addition of magnesia.

The magnesium of the original silicates, which is changed to carbonate in the zone of katamorphism, goes through the same processes of distribution as the calcium carbonate. A part of it passes down into the belt of cementation, and is there precipitated in dolomite, ankerite, parankerite, and hydrous magnesium silicates. But a large part of the magnesium salts, before or after an underground journey, join the surface streams and find their way to the ocean. Magnesium is there precipitated on a great scale as carbonate, not by the reaction of organisms, but by the reaction of magnesium salts in solution upon the calcium carbonate previously precipitated by organisms. This process inaugurated in the sea is continued in the carbonate formations on the land. This involves a substitution of mag-

nesium for calcium, or else abstraction of much calcium, or both. It is plain that the magnesium which occurs in the sedimentary rocks as magnesium carbonate is largely introduced by the substitution of magnesium for previously precipitated calcium.

When the sedimentary rocks and the altered original rocks of the zone of katamorphism containing the secondary magnesium minerals pass into the zone of anamorphism the original magnesium minerals, viz, the pyroxenes, amphiboles, micas, and olivines, may be produced; but a part of the magnesium goes into other minerals. Of these the garnets appear to be the most important, and some of the subordinate minerals are chondrodite, humite, clinohumite, tourmaline, and melilite.

It is a well-known fact that in mechanical sedimentary rocks metamorphosed in the zone of anamorphism the amphiboles are developed upon a much greater scale than the pyroxenes, and that the magnesium-bearing mica, biotite, forms very abundantly. This is a natural consequence of the depletion of the mechanical sediments in calcium as compared with the original rocks. The amphiboles are much more heavily magnesian than the pyroxenes. For instance, in tremolite the magnesium-calcium ratio is 3:1, whereas in diopside it is 1:1. Consequently from the mechanical products in which the magnesium is somewhat concentrated and the calcium depleted there is a tendency to produce the magnesian minerals, amphibole, and biotite. But in the development of amphiboles and pyroxenes the pressure and the specific gravities of these minerals are also concerned. (See pp. 278–280.)

SODIUM.

Sodium, according to Clarke's estimate of 1891, composes 2.28 per cent of the outer 10 miles (16.1 kilometers) of the crust of the earth, including the original rocks, the hydrosphere, and the atmosphere. According to this estimate it composes 1.14 per cent of the hydrosphere and 2.36 per cent of the lithosphere. In his estimate of 1900 the amount of sodium in the original rocks is increased to 2.63 per cent. Sodium thus has sixth place among the elements. Reckoned as an oxide Clarke's estimate for 1891 is 3.20 per cent and for 1900 it is 3.55 per cent, and of oxides it stands sixth.[a]

[a] Clarke, cit., Bull. 78, p. 39; Bull. 168, p. 15.

Sodium is a constituent of many of the minerals of the original igneous rocks. These minerals comprise the feldspars, the nephelites, cancrinite, sodalite, haüynite, noselite, and marialite. In the meteorites sodium is reported only in the feldspars. Because of the dominating importance of the feldspars[a] the larger part of the sodium occurs in them, although the sodalite and nephelite groups of minerals are important sources of the element. Sodium is so abundant in the acid plagioclases as to give them the name of soda feldspars.

In 78 shales soda composes 1.31 per cent; in 624 sandstones, 0.61 per cent, and in 843 limestones, 0.34 per cent. It thus appears that in the shales the amount of soda is reduced to only about one-third of that in the original rocks, in the sandstones to about one-sixth, in 345 limestones not used for building purposes[b] to a minute fraction, but in 498 limestones used for building purposes to about one-sixth. (See p. 938.)

Multiplying the percentages of soda in each of the classes of sediments by their masses and taking their sums we have the average percentage of soda in the sediments, thus:

$$1.31\times.65+.61\times.30+.34\times.05=1.0515.$$

Since the soda in the original rocks is 3.55 per cent, the deficiency in the sediments is 2.4985 per cent. It thus appears that the deficiency in the sediments considered is about 70.38 per cent of the total amount of soda in the original rocks. For the entire weight of the sediments this gives a deficiency of 475,065,000,000,000,000 metric tons.

It is possible that when more analyses have been made of sedimentary rocks the estimates of soda in them may be somewhat increased, but since the analyses show the amount of potassium to accord fairly well with that of the original rocks (see p. 1000), it does not seem probable that much of the deficiency in soda can be explained by insufficient analyses.

The natural source to which one immediately turns to account for this vast deficiency is the ocean. The actual amount of sodium in the ocean, as determined from Dittmar's estimates, is 14,180,000,000,000,000 metric tons, which, reckoned as an oxide, would be 19,101,000,000,000,000 metric tons. While sodium is the most abundant element in the ocean with the exception of chlorine, and is more than five times as abundant as the magnesium,

[a] Clarke, cit., Bull. 168, p. 16.

[b] Clarke, cit., Bull. 168, pp. 16–17.

potassium, and calcium together, it is seen that this amount is trivial as compared with the total deficiency in the sedimentary rocks, being indeed only 4.02 per cent of this amount. It is therefore plain that, as in the case of magnesium, we must turn to some other direction to account for the great deficiency of sodium in the ordinary sedimentary rocks. The natural direction to which to turn is to the salt deposits of the world. Many great salt deposits have been discovered in the United States, Europe, and other parts of the world; such deposits are illustrated by those of Poland, New York, and Louisiana. Doubtless many other salt deposits exist which have not been discovered. Moreover it is known that there are extensive salt deposits below lakes such as Great Salt Lake and the Dead Sea. No attempt has been made to quantitatively determine the mass of the salt deposits. Until this is done no statement can be made as to the proportion of the deficiency of sodium in the ordinary sedimentary rocks which such sediments will account for.

Finally, as is shown on pages 541–543, in arid regions sodium salts are largely retained in the deposits of the belt of weathering. Since sodium-bearing deposits are known to be very thick in various arid regions, such, for instance, as those in the western part of the United States, the amount of sodium thus accounted for is very great, but as yet our knowledge is not sufficiently advanced to make any quantitative estimate of it.

From the foregoing it appears highly probable that we must look to the salt deposits and to the alkaline deposits of arid regions to explain the great deficiency of sodium in the ordinary sediments rather than to the ocean. If this conclusion be correct, calculations upon the age of the earth have no value which are based upon the derivation of salt from the land through weathering processes and its accumulation in the sea, and which ignore or place as relatively unimportant the salt deposits of the land. Such calculations furnish but another illustration of the danger of considering a single factor in a series of complex geological processes, and neglecting to ask the question whether there are other equally or more important factors concerned.

When the original rocks containing sodium-bearing minerals are decomposed in the zone of katamorphism, the larger part of the sodium passes into solution, contrasting in this respect, as will be seen, in a marked

degree with potassium. During the underground journey of a part of the solutions a small portion of this sodium is deposited in the belt of cementation. The sodium-bearing minerals formed by direct alteration in the zone of katamorphism, and those there deposited as cementing minerals, are substantially the same and are mainly the zeolites. The more important of these zeolites containing sodium in notable quantities are thomsonite, hydronephelite, natrolite, mesolite, analcite, stilbite, and gmelinite.

So far as rocks containing sodium in the zeolites pass into the zone of anamorphism some of the original minerals of which sodium is a constituent may be reproduced, but manifestly the amount of such minerals will be small as compared with the amount of the original sodium-bearing minerals in the rocks. Corresponding with this fact the rich sodium minerals, nephelite, cancrinite, sodalite, haüynite, and noselite, have never been reported as anamorphic minerals of the sedimentary rocks. Most of the sodium present passes into the feldspars; but where the rocks have been so far decomposed as not to leave a large quantity of the original sodium-bearing minerals, the amount of sodium is not sufficient to produce any considerable proportion of the feldspars. In consequence, as pointed out on pages 899–904, the schists and gneisses which form from pelites only exceptionally contain any considerable quantity of soda feldspars. The dominant secondary minerals which are produced are quartz and mica. However, in the psephites, in which the processes of decomposition are not far advanced, and in which the sodium is therefore relatively abundant, considerable quantities of soda feldspars are produced during recrystallization. But as already noted, even in those sedimentary rocks in which residual soda is present in the undecomposed original minerals, it appears that it is not known to have been anywhere so abundant that the peculiar minerals known as the soda-bearing minerals, such as nephelite, sodalite, etc., are produced.

POTASSIUM.

According to Clarke's estimate of 1891 potassium composes 2.23 per cent of the outer 10 miles (16.1 kilometers) of the crust of the earth, including the original rocks, hydrosphere, and atmosphere. Of the ocean it composes 0.04 per cent, and of the original rocks 2.40 per cent. In his estimate of 1900 Clarke reduces the figure for the original rocks to 2.32

per cent. This gives potassium eighth place in abundance among the elements. Reckoned as an oxide the amount in the original rocks, according to Clarke's estimates of 1891 and 1900, is 2.90 and 2.80 per cent, respectively.[a] As an oxide, potassium thus has seventh place.

Potassium is an abundant constituent of a number of the silicates of the original rocks. The more important of these are the feldspars and the leucites. Since the feldspars probably compose more than half of all the original rocks (see p. 937), the chief original sources of the potassium are the feldspars. Of the feldspars the content of potassium is so great in orthoclase and microcline as to give them the distinctive name potash feldspars, thus discriminating them from the acid end of the plagioclase series in which soda is the dominant alkali.

Considering the secondary rocks, the amount of potassa in 78 shales is 3.25 per cent,[b] in 624 sandstones 1.24 per cent, and in 843 limestones 0.46 per cent. It thus appears that as compared with the original rocks, the amount of potassa in the shales is increased by about one-fifth, in the sandstones is reduced to less than one-half, and in the limestones to less than one-fifth. Multiplying the percentage of potassa in each class of sediments by the volume of those sediments, and taking their sum, we have the average amount of potassa for the sediments considered, thus:

$$3.25 \times .65 + 1.24 \times .30 + .46 \times .05 = 2.5075.$$

Since the amount of potassa in the original rocks as given by Clarke in his latest estimate is 2.80 per cent, we have a deficiency of potassa in the sediments of 0.2925 per cent, or 1,974,375,000,000,000 metric tons.

According to Dittmar's estimates the actual amount of potassium in the ocean is 512,000,000,000,000 metric tons, which, reckoned as potassa, is 616,600,000,000,000 metric tons, or 31.23 per cent, i. e. about one-third of the total deficiency. Potassium compounds are also important accessories in salt deposits. For instance, analyses show that the potassium composes from 1.1 to 7.4 per cent of the total solids of Great Salt Lake[c] and 1.478 per cent of the total solids in the Dead Sea.[d]

As is well known, above beds of rock salt there are not infrequently overlying beds rich in potassium and magnesium. This class of salts is well

[a] Clarke, cit., Bull. 78, p. 39; Bull. 168, pp. 14–15.
[b] Clarke, cit., Bull. 168, p. 17.
[c] Mon. U. S. Geol. Survey, vol. 1, pp. 253.
[d] Encyclopedia Brittanica, 9th ed., 1877.

illustrated at Stassfurt, where, as already noted (p. 994), from 1876 to 1880 the amount of carnallite ($KMgCl_3.6H_2O$), kieserite ($MgSO_4+H_2O$), and kainite ($MgSO_4.KCl+3H_2O$) mined was 699,136 metric tons, whereas the amount of rock salt was for the same years only 96,856 metric tons. Since the salt deposits are so important, it follows that the total amount of potassium in such deposits is large.

It seems probable that the potassium in the salts of inland seas and in the saline deposits is sufficient to account largely and perhaps fully for the remaining two-thirds of the deficiency of potassium in the sediments.

Where the rocks which contain potassium are altered in the zone of katamorphism, the potassium-bearing minerals do not decompose to the same extent as the sodium-bearing minerals. So far as the potassium is in leucite, it readily alters; but, as already noted, the greater part of the potassium is in orthoclase and microcline, and these are the most difficultly decomposable of the feldspars. These minerals disintegrated and only partially decomposed are carried in great quantities to the sea. But even where the potassium feldspars are decomposed, it seems that the potassium is held in an insoluble form to a large extent. Prestwich[a] attributes the retained potassium to the action of alumina, although he does not explain the reaction by which it is held. Mendeléeff[b] emphasizes the absorptive power of the soil, and especially of the vegetable mold, for potassium. It is known that potassium compounds are used by plants to a much greater extent than sodium compounds. But the influence of plants in retaining potassium can not be cited to explain the apparent concentration of potassium in the muds. It appears to me that where the feldspars have decomposed and the potassium largely remains in the silts and muds, it is likely that this element has passed into the zeolites, especially apophyllite.

When the rocks formed in the zone of katamorphism are buried in the zone of anamorphism, the original minerals which contain the potassium may be produced, but it has already been seen that the chief minerals originally holding the potassium are orthoclase and microcline. It has further been pointed out that the soda minerals are much more readily decomposed and that much less of the sodium is left in the sedimentary

[a] Prestwich, Joseph, Geology—chemical, physical, and stratigraphical, vol. 1, 1886, p. 54.

[b] Mendeléeff, D., The principles of chemistry, translated by Geo. Kamensky, Longmans, Green & Co., London, vol. 1, 1897, pp. 546–547.

rocks. Thus it is that orthoclase and microcline are the chief feldspar minerals which develop by the deep-seated metamorphism of the pelites—rocks in which decomposition has been carried further than in the other mechanical sediments. To a less extent orthoclase is likely to be the dominant feldspar in the other sediments. However, since complete decomposition for the mechanical sediments is very rare, the potassium for much of the orthoclase and microcline which develop by metamorphism is derived from the undecomposed original minerals.

BARIUM, STRONTIUM, CHROMIUM, NICKEL, LITHIUM, FLUORINE, BROMINE.

In Clarke's estimate of 1900 of the lithosphere barium is put down as composing 0.05 per cent, strontium as 0.02 per cent, chromium, nickel, lithium, and fluorine as 0.01 per cent each and bromine as less than 0.01 per cent. The quantities of these elements are so small and so little is known about the transformations through which they go that no attempt is here made to consider the influence of metamorphism upon their distribution.

GENERAL STATEMENTS.

At the beginning of this chapter it is stated that the attempt to apply quantitative methods to the redistribution of the chemical elements is made more with the idea of laying out problems to be solved than with the belief that the calculations approach accuracy. However, when all of the equations which compare the average composition of the sediments with the original rocks are taken into account the impression is gained that the calculated relative proportions of the three classes of sediments discussed—that is, the shales (including all silicate rocks), the sandstones, and the limestones—can not be far from the truth. The percentages of each of the elements in the sediments and in the original rocks are matters of quantitative determination, by imperfect methods, it is true, and so far as absolute masses are concerned the estimates given for the sediments are but roughly approximate, but the relative proportions stated are probably nearer the truth. Other proportions of the sediments than those used might be selected which would answer in the equations for a single element, and possibly some other proportions than those used might be selected which would accord better with the facts; but it seems certain that such proportions could not differ

greatly from those given—0.65 for the shales, 0.30 for the sandstones, and 0.05 for the limestones. While with the numbers used discrepancies have appeared, for the most part they are of a kind which throw light upon the processes of segregation of compounds in materials other than shales, sandstones, and limestones.

In conclusion it is to be remembered that the equations are independent of the estimates of the absolute masses of the sediments, and therefore they can not be said to give any support to the estimates of the average thickness of the sediments for the continental areas, nor to the absolute amounts of the elements which have been calculated to be abstracted from certain of the sediments and segregated in certain others of them.

Certain of the results set forth in the previous pages indicate the possibility that the estimate of the mass of the sediments as 2 kilometers thick for the continental areas is too large, but it will be noted that this estimate is very conservative as compared with estimates made by others. (See p. 939.) If one were to estimate the mass of the sediments as 1 kilometer thick for the continental areas, while the calculated percentages of the deficiencies and excesses of the various elements in the sediments as compared with the original rocks would not be changed, the calculated absolute amounts would be reduced one-half. This would reduce by one-half the calculated percentage of oxygen of the atmosphere required to oxidize ferrous iron (see p. 951), and to oxidize iron sulphide (see p. 952); would divide by 2 the numbers comparing the amount of carbon in the sediments with that in the atmosphere and hydrosphere (see pp. 965–966); and would divide by 2 all absolute estimates of the surpluses and deficiencies of the various elements in the ordinary sediments, as, for instance, the calculated deficiency in iron. (See pp. 987–988.) Other similar changes would be made in the calculations. These facts may be regarded by some geologists as evidence that even the moderate estimate for the sediments of 2 kilometers thick for the continental areas is too great, and with this view I am inclined to agree.

CHAPTER XII.

THE RELATIONS OF METAMORPHISM TO ORE DEPOSITS.[a]

PART I. GENERAL PRINCIPLES.

INTRODUCTORY.

The principles of metamorphism, discussed somewhat fully in the previous chapters, have a direct bearing upon ore deposits, as it will be shown in this chapter that the deposition of most ores is but a special case of metamorphism of exceptional interest to man. Through the preceding chapters are scattered the principles applicable to ore deposits; but as many persons interested in ores may not care to study in detail all the principles which concern metamorphism, it seems advisable to give here a brief summary of the more important principles and conclusions directly applicable to ore deposits. In order not to make the extension too great, only the principles will be repeated; for evidence showing their correctness the reader may turn to the previous chapters.

From this discussion are excluded all the nonmetallic economic products which are used without reduction to the metallic form, as apatite, clay, salt, etc., and the very rare and unimportant metals. Thus the treatment is confined to those important ores the metals of which are commonly used in the metallic rather than in the combined form. Thus circumscribed, the chapter is chiefly restricted to ores of iron, aluminum, cobalt, nickel, manganese, lead, zinc, copper, tin, mercury, silver, gold, and platinum. Arsenic, antimony, bismuth, chromium, molybdenum, and tungsten are not considered at all, or are only incidentally mentioned.

[a] This chapter in a less mature form was published in time for distribution at the Washington meeting of the American Institute of Mining Engineers in February, 1900, as a pamphlet of 126 pages. A revised pamphlet edition of 151 pages was published during the summer of 1900. This edition appears as pages 27 to 177 of Volume XXX of the Transactions of the American Institute of Mining Engineers. This paper was republished in 1902 by the Institute in the special volume upon the Genesis of ore deposits, pages 282–432, which volume contains also a closing discussion under the same title, pages 763–781.

CLASSIFICATION OF ORE DEPOSITS.

Ore deposits may be divided into three classes upon the same basis as are the three great divisions of rocks:

(1) Ores produced by the processes of sedimentation, or sedimentary ores.

(2) Ores produced by igneous processes, or igneous ores.

(3) Ores produced by the processes of metamorphism, or metamorphic ores.

Since this volume is a treatise upon metamorphism and not upon physical geology in general, only the third class of ores, those produced by metamorphism, come within its scope. But ores formed by processes of sedimentation and by igneous processes will be briefly considered, mainly in order to point out their relations to ores produced by processes of metamorphism.

Before taking up the ores it is necessary, as already stated, to summarize certain parts of the previous chapters. The three great divisions of the processes of modifications of rocks which most intimately concern ore deposits, and therefore need to be summarized, are:

The deformation of the lithosphere.

Volcanism.

The circulation and work of solutions.

DEFORMATION OF THE LITHOSPHERE.

In another place I have shown that the outer part of the crust of the earth may be divided into three zones, depending upon the character of the deformation—(1) an upper zone of rock fracture, (2) a middle zone of combined rock fracture and flowage, and (3) a lower zone of rock flowage.[a] In Chapter IV it has been shown that the zone of fracture corresponds to the zone of katamorphism and that the zone of flowage corresponds to the zone of anamorphism.

ZONE OF FRACTURE, OR ZONE OF KATAMORPHISM.

The zone of fracture is that near the surface and in it the rocks are deformed mainly by macroscopic fracture. The ruptures are those of faulting, jointing, bedding parting, fissility, and brecciation. The rocks

[a] Van Hise, C. R., Principles of North American pre-Cambrian geology: Sixteenth Ann. Rept. U. S. Geol. Survey, pt. 1, 1896, p. 589.

are adjusted to their new positions mainly by differential movements between the separated parts. The so-called folds in the zone of fracture are largely the result of numerous parallel joint fractures across the strata with small angular displacements at the joints, giving each block a slightly different position from those on either side, and thus as a whole making joint folds. For instance, the folds of the rigid rocks in the Alleghenies are not in the main true flexures, but a series of slightly displaced blocks.

It is shown on pages 189–190 that, making all the assumptions in favor of as great a thickness as possible, the maximum thickness of the zone of fracture can not be greater than 10,000 or 12,000 meters. In many cases, even for the strongest rocks, deformation frequently takes place by flowage at depths not greater than one-third to one-half of 10,000 meters. For the weaker rocks deformation by flowage may take place at very moderate depths. If the conclusions above given be correct, it follows that all open fissures must disappear at moderate depths, and that the maximum depth at which they can exist is the depth of the zone of fracture for the strongest rocks. Illustrations of the disappearance of fissures with depth are known at various places. In the gold belt of the Sierra Nevada, as Lindgren says, it is "an incontestable fact that many small veins close up in depth."

The dying out of fissures below is insisted upon in order to exclude the hypothesis of filling of fissures from the bottom. If fissures gradually decrease in size and finally die out, the streams which make their way into the fissure must enter from the sides or from above. For further development of this point see pages 1069–1072.

OPENINGS OF ZONE OF FRACTURE.

It has been shown that the zone of fracture is characterized by openings. It will be seen that the nature of the openings in the rocks is of the greatest importance in the formation of ore deposits. It is therefore necessary to summarize the material given in Chapter III upon this subject.

It is there shown that the openings of rocks deserve consideration from three points of view: The form and continuity of the openings; the size of the openings; and the volume of the openings, or the pore space.

FORM AND CONTINUITY OF OPENINGS.

The openings in rocks include those which are of great length and depth, as compared with their width, and thus are essentially flat parallelopipeds; those in which the dimensions of the cross sections of the openings are approximately the same, and therefore resemble tubes of various kinds; and those which are irregular.

The openings which have great length and depth as compared with their width are those of faults, of joints, of bedding partings, and of fissility. The order mentioned is that of continuity. As to position, bedding partings are parallel to previous structures; while faults, joints, and fissility are at various angles with the bedding parting, and therefore intercept the layers. Because of this fact, these forms of openings may connect separated porous strata. This is more likely to be true of faults than of joints, and of joints than of fissility.

The openings in which the dimensions of the cross section are approximately the same are those in mechanical deposits, such as conglomerates, tuffs, sandstones, and shales. From the point of view of ore deposits the most important characteristic of the openings of this class is that they are continuous, and therefore any part of a coarse, uncemented mechanical deposit is connected with all other parts by openings.

Irregular openings are those of the vesicular lavas, and the irregular fractures of rocks. The openings of the lavas are usually variable in magnitude, and are discontinuous. Usually single irregular fractures are of limited extent, but many fractures may be concentrated along a zone, and a composite zone may be continuous for long distances.

Openings of any of the above classes, whether produced by deformation, by original sedimentation, or by volcanic action, may be enlarged by solution. This will be the case wherever the processes of solution more than counterbalance the processes of deposition, and, as later explained, is more likely to occur with downward-moving water than with upward-moving water. Since downward-moving waters are dominant above the level of ground water, and are prominent in the upper part of the belt of cementation, it is in this area that openings are most frequently enlarged by solution.

It has been argued by Posepny that openings serving as channels for ground water may be produced wholly by solution. That openings may be somewhat prolonged and adjacent opening connected by solution,

thus helping underground circulation, is more than probable, but that long and important passages are produced wholly by solution is an assumption which I think has not been verified.

SIZE OF OPENINGS.

Openings in rocks may be divided, upon the basis of size, into those larger than capillary size, or supercapillary openings; capillary openings; and those smaller than capillary size, or subcapillary openings. The magnitudes of these openings are given on pages 134–137. The openings of bedding parting, of faults, of joints, of conglomerates, and of tuffs are frequently of supercapillary size. Many of these openings, and also many of those of the sandstones, are of capillary size. All classes of openings may be somewhere of subcapillary size, but many rocks, such as massive igneous rocks and shales, may contain only subcapillary openings.

VOLUME OF OPENINGS.

The total volume of the openings is dependent upon the number and the size. The amount of pore space in rocks varies from less than 1 per cent to more than 50 per cent. The total volume of the openings in a rock in which they are so small as to be almost imperceptible and all subcapillary may be as great as in a rock in which many openings are seen. For instance, the pore space of a chalk may be as great or greater than that of a sandstone or of a massive rock containing numerous continuous fracture openings of large size. (See pp. 124–125.) In such cases the small size of the openings is compensated by their vast numbers.

CHEMICAL REACTIONS.

As explained in the preceding chapters, especially in Chapter IV and more fully in Chapters VII and VIII, the reactions of the zone of fracture, or katamorphism, are those of oxidation, carbonation, hydration, solution, and deposition. All are of great importance in connection with ore deposits. In the belt of weathering all of these reactions, with the exception of deposition, are vigorous. The sulphides, including the metals and the sulphur, are likely to be oxidized. Oxides may be further oxidized. The metals may be carbonated and hydrated and are likely to be dissolved upon an extensive scale. While all of these reactions take place in the belt of

cementation, oxidation is frequently confined to those parts of the belt in which the waters come somewhat directly from the surface; whereas deeper, especially where the percolating waters have come into contact with organic compounds or sulphides, the waters may become reducing, and partial or complete deoxidation of the valuable metals take place. Furthermore, while solution probably occurs to a greater extent than deposition in the belt of cementation, as explained on pages 629–640, material is continually deposited in the openings of the belt, and the rocks are cemented in consequence of the expansion reactions of oxidation, carbonation, and hydration, and in consequence of selective precipitation, of intrusion, and of other phenomena.

ZONE OF COMBINED FRACTURE AND FLOWAGE.

Deformation by combined fracture and flowage takes place in a middle zone because the rocks of a given part of the lithosphere vary in character, temperature, moisture, speed of deformation, etc. (See pp. 766–768.) Of these factors producing combined fracture and flowage, the effect of the character of the rocks is most obvious. While very considerable rock masses, such as the limestones and quartzites, may be homogeneous, heterogeneity is the rule. The sedimentary rocks are composed of laminæ, layers, beds, and formations, no one of which is exactly like the adjacent one. The massive igneous rocks contain minerals of different resisting power, the particles of which are of different sizes. In consequence there is a broad zone in which the deformation may be by combined fracture and flowage. For instance, in an interbanded slate and graywacke the slate bands may be deformed by flowage and the more rigid graywacke bands be deformed largely by fracture. In an interbedded limestone and clastic series the limestones may be deformed mainly by flowage and the clastic material mainly by fracture. In many cases the change from one kind of deformation to the other is amazingly sharp, the more resistant bands being intersected by innumerable fractures which stop abruptly at the bands where the rock is deformed by flowage. The deformation of a massive rock mainly by flowage, but in a subordinate way by fracture, is finely illustrated by the Berlin rhyolite-gneiss described by Weidman.[a] The deformation of this rock was mainly by recrystallization, but many of the

[a] Weidman, S., A contribution to the geology of the pre-Cambrian igneous rocks of the Fox River Valley, Wisconsin: Bull. Wis. Geol. Nat. Hist. Survey, No. 3, 1898, pp. 32–47.

mineral particles were fractured into several pieces, or even granulated. Between the larger pieces of the feldspar minute openings formed. Many minute joints and crevices also were produced and were subsequently filled by cementations.

The marked effect which the character of the rock may have upon the nature of the fractures is well illustrated in the Cripple Creek district, where, according to Penrose, in the hard rocks the fissures are sharp, clean-cut breaks, while in the soft rocks they are ordinarily a series of very small cracks, constituting a displacement of a kind which I call a distributive fault. Mines which are partly in hard and partly in soft rock illustrate this, as the following extract from Penrose will show:[a]

> The vein on which the Buena Vista, Lee, Smuggler, and Victor mines are located occupies a sharp, clean-cut fissure, partly in the massive rock and partly in the hard breccia; but when it passes into the soft, tufaceous breccia on the east slope of Bull Hill the fissure is represented only by faint cracks occupied by no vein of importance. In this case the force which caused the fissure overcame the cohesion of the harder rock sufficiently to make a clean break, but in the more plastic rock it overcame cohesion only to the extent of causing a series of faint fractures without any one well-defined break.

It follows from the above that displacement may disappear at variable depths. Where there are fractures with large displacement they are likely to extend to very considerable depths, and in proportion as the displacement is small they are likely to disappear at less depths. Thus the depths to which displacements extend depend largely upon the character of the rocks. For instance, in a region in which there is a shale formation at moderate depth underlying brittle rocks, strong fissures in the higher formations may disappear as they encounter the shale, being there replaced by flexures. Where formations of shale are between brittle formations fissures may cease at the top of the shale and other fissures appear below it. Thus may fissures not only die out below, but may disappear above, the fault along the fissures being replaced by a flexure in the shale, which yields by flowage. This is beautifully illustrated by the Enterprise mine, of Rico, Colo., described by Rickard and Ransome (see fig. 29, p. 1208), where faulted fissures in sandstone and limestone disappear at the place where shale is encountered, the shale accommodating itself to the fractures below by monoclinal flexures. (See p. 1204.)

[a] Cross, Whitman, and Penrose, R. A. F., Geology and mining industries of the Cripple Creek district, Colorado: Sixteenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1895, p. 144.

From the above it appears that openings of the zone of the combined fracture and flowage comprise all of the classes of openings characteristic of the zone of fracture. There is, however, the great difference that upon the average the supercapillary openings are smaller, less continuous, and less numerous than in the zone of fracture.

Since there is such a great variation in the strength of the rocks and in other factors, the belt of combined fracture and flowage may be of considerable thickness, possibly as thick as 5,000 meters. In this zone we have all combinations of the phenomena of fracture in the various ways above mentioned, and of flowage by granulation and recrystallization.

ZONE OF FLOWAGE, OR ZONE OF ANAMORPHISM.

In the zone of rock flowage deformation is chiefly by granulation and recrystallization, few openings being produced, except those of microscopic size. (See pp. 658–659, 673–675, 685 et seq.) This conclusion rests upon arguments which can not here be fully repeated.[a] However, it may be said in passing that the conclusion that a zone of rock flowage exists at moderate depth is based, first, upon deduction from known physical principles as to the behavior of solid bodies under pressure; and, second, upon observation. It is well known that when a rigid body, such as a rock, is subjected to unequal stresses in various directions and the difference in the stresses is greater than its ultimate strength under the conditions in which it exists, it must rupture or flow. If a rock be subjected to a stress in a single direction greater than its ultimate strength in that direction, and the rock is not under pressure in other directions, rupture occurs. However, if we suppose that the rock be subjected to stresses greater than the ultimate strength of the rock in all directions, and that the difference in the stresses in different directions is greater than the ultimate strength of the rock under the conditions in which it exists, then if openings could be produced by rupture, they would be closed by pressure. In other words, at a certain depth below the surface of the earth, if we could suppose that cracks and crevices are formed by the deformation to which the rocks are subjected, the pressures in all directions being greater than the ultimate strength of the rock, these cracks and

[a] Van Hise, C. R., Principles of North American pre-Cambrian geology: Sixteenth Ann. Rept. U. S. Geol. Survey, pt. 1, 1896, p. 594 et seq.

crevices would be closed. The rate of closing would depend upon many factors. (See pp. 766–768.)

Since this conclusion was reached, Adams and Nicolson[a] have actually deformed marble under the conditions supposed to exist at moderate depth, with the result that the rock changed its form with no perceptible openings.

Before the above inductive reasoning or Adams and Nicolson's experiments were made, I had become convinced from observation that at moderate depth rocks are deformed with fracture and differential movements between the solid particles (granulation), and by continuous solution and redeposition by underground water (recrystallization).

It has been explained (pp. 189–190) that the maximum possible depth of the zone of fracture for the strongest rocks under quiescent conditions is not greater than 10,000 or 12,000 meters, and that for the majority of rocks, and especially under conditions of movement, the zone of flowage is probably reached at depths much less than this.

OPENINGS OF ZONE OF FLOWAGE.

The openings of the zone of flowage are dominantly subcapillary. Capillary openings are numerous, but they are not usually continuous for any considerable distance. Supercapillary openings may exceptionally exist in the upper part of the zone of flowage in consequence of very rapid deformation, but such openings are likely to be temporary, for when rapid deformation ceases they are closed by flowage.

REACTIONS OF ZONE OF FLOWAGE.

The chemical reactions of the zone of anamorphism, as fully explained in Chapters IV and VIII, are dominantly those of silication, dehydration, deoxidation so taking place as to decrease volume.

RELATIONS BETWEEN ZONES OF DEFORMATION.

From the preceding pages it is clear that the zones of fracture, of combined fracture and flowage, and of flowage are not sharply separated from one another.

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[a] Adams, F. D., and Nicolson, J. T., An experimental investigation into the flow of marble: Phil. Trans. Roy. Soc. London, ser. A, vol. 195, 1901, pp. 363–401.

It is highly probable that upon the average the openings of the zone of fracture gradually decrease in number and size as depth increases, until in the zone of flowage the openings are, as already explained, microscopic or nonexistent. If such a gradation exists, it is a necessary corollary that the deformations of the zone of fracture must have their equivalents in the deeper-seated zone of flowage. This point is fully discussed elsewhere.[a] It is explained that with depth, faults are replaced by flexures, and that any deformation of a large mass of a given rock from one form to another by fracturing may be imitated by similar changes of form in the zone of flowage, the result being there accomplished by granulation of the mineral particles or by their recrystallization, or by both.

Where rocks have been deformed in the zone of flowage and are now at the surface there is superimposed upon the effects of the deep-seated deformation the deformation by fracture resulting from earth movements during the time the rock was slowly migrating through the zone of fracture to the surface.

EFFECTS OF DEFORMATION AND CHEMICAL CHANGES UPON TEMPERATURE.

It has been pointed out in previous chapters that deformation results in the liberation of heat which may considerably raise the temperature of the rocks. Indeed, Mallett holds (see pp. 99–100) that deformation may actually produce enough heat to fuse the rocks. While I dissent from this conclusion, this view illustrates the importance of the rise of temperature which may follow from mechanical action.

It has been shown further that a moderate rise in temperature may increase the activity of the solutions to an amazing extent. Indeed, in a chemical laboratory a slight rise in temperature is often sufficient to inaugurate a reaction which otherwise would not take place, and to increase the speed of the reaction many fold. It is therefore clear that deformation is favorable to the segregation of ore deposits in two different ways, first, by forming openings for a vigorous circulation, and second, by heating the solutions and thereby greatly increasing their activity.

In the zone of katamorphism the chemical reactions liberate heat, cause an increase of temperature in the zone in which the ores are mainly segre-

[a] See Chapter VIII (pp. 776 et seq). See also Principles of North American pre-Cambrian geology, cit., pp. 674–676, 694–698.

gated, and therefore help to develop the ores. Thus, in this zone, deformation and chemical reactions both favor the concentration of ores. In the zone of anamorphism the chemical reactions absorb heat, and to that extent work against the effect of deformation.

In the western portion of the United States there have been recent orogenic movements and also recent development of ore deposits. But correlative with orogenic movements is volcanism, and it is pointed out in the following section that volcanism also, for various reasons, is favorable to the segregation of ores. It is therefore exceedingly difficult in any given region to determine the relative quantitative importance of orogenic movements and volcanism in the development of the ores. Until this study is seriously taken up for extensive regions the relative importance of the two must remain largely a matter of speculation.

VOLCANISM.

The great importance of volcanism in reference to metamorphism has been fully dealt with in the previous chapters. The vast extent and great thickness of the Tertiary volcanic rocks afford evidence of the prodigious quantities of material which may be extruded in a single geologic period. It has been explained that correlative with and below these extrusions probably occurred intrusions on an even vaster scale. It has also been seen that important volcanism and extensive orogenic movements are usually simultaneous in the same regions. The relation between the two is that of cause-effect. Orogenic movements produce numerous openings, which extend deeper than those that exist under quiescent conditions. These are taken advantage of by the intrusive rocks which are being forced toward the surface. The enormous hydrostatic pressure of the upwelling lava is also one of the factors in further fracturing. Consequently there is action and reaction between orogenic movements and volcanism, each advancing the other.

Volcanism may promote the development of ore deposits in various ways.

First. The igneous rocks may furnish metals for the ores. In the case of a given ore deposit the metal may be almost wholly derived from the recent igneous rocks, almost wholly from earlier rocks surrounding the later intrusion, or partly from the two sources. Illustrations will be given later.

Second. The igneous rocks may furnish aqueous and gaseous solutions which transport the metals to their places of deposition. It is very difficult to determine the quantitative amount of the solutions of this sort. Where the igneous rocks are intruded in the zone of fracture, or appear at the surface in the ordinary forms characteristic of volcanism, it is impossible to discriminate the gaseous and aqueous material which has always been within the magma from the solutions which have derived their water from meteoric sources or from the sea. It is certain that vast quantities of water of meteoric origin pass into the zone of fracture. In connection with the water phenomena of volcanic action it may perhaps be doubted if the water from the sea is important; but there can be no question concerning the effect of water of meteoric origin. Where voluminous hot springs issue in connection with present or past volcanic action all the evidence indicates that the major portion of this water is of meteoric origin (pp. 1065–1069). However, it has been pointed out (pp. 661–668) that in the zone of anamorphism the conditions are very different. It can not be assumed that there the water is abundantly derived from meteoric sources. In connection with batholitic action it has been shown that there is complete gradation between strictly igneous material and material which is apparently deposited from solutions. It has been explained that the water which does this work is probably in considerable part derived from the magma itself, although some is doubtless included between the mineral particles and some is produced by processes of dehydration. But even for this zone it is impossible to make any quantitative statement as to the relative amounts of water concerned in the segregation of ores which is derived from emanation of original magmas and from other sources.

Third. The heat of the igneous rocks may render the solutions vastly more active in segregating the metals from the intruded rocks. The amazing increase in the power of solutions to dissolve material in consequence of rise of temperature has been emphasized (pp. 79–81). The meteoric solutions adjacent to the igneous rocks must be at a much higher temperature than normal; therefore their activity is increased many fold. It follows that where the solutions in sedimentary, metamorphic, or ancient igneous rocks may not be sufficiently active to segregate the ores even where the metal exists in sufficient quantity, they may so gain in their segregating power in consequence of igneous intrusions that ore deposits

develop. This heating of solutions in the surrounding strata by igneous rocks is believed to be a factor of the most pronounced importance in the segregation of many ore deposits.

Fourth. The introduction of the igneous rocks may promote fracturing and thus open channels for circulation. Also, after an igneous rock has crystallized it continues to cool and to contract. In consequence of its contraction trunk channels may be opened along the contact of the intrusive and intruded rock and within the igneous mass. The production of openings is very favorable to the segregation of ores.

Fifth. Another important function of the igneous rocks is to furnish impervious basements which control the trunk channels of circulation, as, for instance, in the Lake Superior region, in the Leadville and Tenmile districts of Colorado, and in the Mercur district of Utah.

The formation of a given ore deposit with the aid of igneous rocks may be a consequence of any combination of the above factors, and the relative importance of each factor is variable in different cases. In a given district the determination of the quantitative importance of each of these factors is a problem of great difficulty, but one of great economic importance and scientific interest.

The effect of igneous rocks in the production of ore deposits is different in the zone of fracture and the zone of flowage. In the zone of fracture, as has been fully pointed out, the igneous rocks follow the openings toward the surface, and when they finally reach the surface are spread out over it.

In the zone of fracture the effects of igneous rocks in the belt of weathering and in the belt of cementation need separate consideration. In the belt of weathering, above the level of ground water, intruded rocks are baked or calcined. They are steamed by the gaseous solutions. It is possible that in this belt ore deposits may be segregated through the influence of volcanism, but positive evidence that this is a fact is lacking.

In the belt of cementation the igneous rocks are of great consequence. There is here the direct effect of heating the intruded rocks, but far more important than this is the indirect effect in heating the solutions. Where the temperature rises above the critical temperature of water the solutions are gaseous. It is, however, believed that the gaseous solutions are probably closely confined to the borders of the intrusive masses. The chief effect is believed to be in reference to the aqueous solutions. It will be

seen that if gaseous solutions are produced in the belt of cementation, where the openings are numerous and the rocks are saturated, there is a strong tendency for the gaseous solutions to condense (see pp. 1019–1020). In this we doubtless have the partial explanation of the dominance in the belt of cementation of ore deposits, which show all the evidence of having been deposited by aqueous solutions, although many such ore deposits are contiguous to igneous rocks.

In the zone of flowage the conditions for intrusions and their effects upon ore deposits are very different from those in the zone of fracture. It has been pointed out that in the zone of flowage the igneous rocks make their way by elevating and thrusting the intruded rocks aside, by actually mashing them so as to shorten their diameters at right angles to the intrusives, and finally by breaking across their structures. The effect of the igneous rocks is both direct and indirect, as in the zone of fracture. The direct effect is the heating of the surrounding rocks, their absorption to some extent, and occasionally even their local fusion. The indirect effect is of far greater consequence. In this deep-seated zone, where the amount of water is small and the openings are usually small and discontinuous, it is highly probable that the solutions are largely gaseous. In all but the upper parts of this zone the natural increase of temperature, due to depth alone, is sufficient to raise the solutions above the critical temperature of water, and thus produce gaseous solutions. Where igneous rocks are present in large quantity and contribute heat it is little short of certain that gaseous solutions are abundant. Therefore it is believed that gaseous solutions, comparatively unimportant in the zone of fracture, are of great importance in the zone of flowage (see pp. 1020–1021).

CIRCULATION AND WORK OF SOLUTIONS.

Solutions in rocks occur in two forms, gaseous solutions and aqueous solutions. Where the underground solutions are referred to without qualification there is no implication as to their state, and they may be as either one or the other, or partly both. Oftentimes for aqueous solutions the term water is used, but in such usage it is not meant to imply that the water is pure. It has been shown (pp. 146–152) that the general forces producing circulation of solutions are gravity, heat, mechanical action, and molecular attraction. These forces act very differently and do not have the same

relative importance in gaseous and aqueous solutions. Therefore the two classes are considered separately. It will be seen that in the belt of cementation aqueous solutions are probably of predominating importance and gaseous solutions very subordinate, and that in the zone of anamorphism gaseous solutions are of dominating importance and aqueous solutions subordinate or unimportant.

CIRCULATION OF GASEOUS SOLUTIONS.

The general circulation of gaseous solutions is a function of the amount of gaseous solutions, of the absolute temperature of the gaseous solutions, of the amount of aqueous solutions adjacent, of gravity, and of the form, continuity, size, and amount of the openings.

The general principle which controls the movement of gaseous solutions is that the gases move from places of high pressure to places of low pressure. The expansive force of a given amount of gas in a given volume is directly proportional to its absolute temperature. Other things being equal, gaseous solutions tend to pass from places of high temperature to places of low temperature. The higher the temperature the greater its expansive power, and the more forceful its movement toward places of low temperature. Therefore heat is a fundamental force in the circulation of the gaseous solutions. Gravity, of the very greatest importance for aqueous solutions, is of importance also for gaseous solutions. So far as gravity is concerned, the same principles apply to gaseous solutions and aqueous solutions. The heavier column of gas pulled by gravity descends and the lighter column is forced to rise. Where the columns are of equal length that of lower temperature descends and that of higher temperature rises.

The circulation of gaseous solutions in the zone of fracture and in the zone of flowage is very different. Moreover, the circulation in the belt of weathering is different from that in the belt of cementation.

CIRCULATION IN BELT OF WEATHERING.

In the belt of weathering the law of gravity practically controls the circulation. Where the temperature of the gases is higher than normal they rise, being driven up by the greater pressure of the adjacent cooler air. Thus, above the level of the ground water, wherever heated gaseous solutions are produced they rise in columns of steam, as in the case of fumaroles and solfataras and in connection with volcanic action.

CIRCULATION IN BELT OF CEMENTATION.

In the belt of cementation the conditions are very different. Here the openings in the rocks are normally occupied by aqueous solutions. However, adjacent to igneous masses gaseous solutions may be produced either as emanations from the igneous rocks or by the heating of the solutions of the intruded rocks above their critical temperature, or by both combined. The surrounding rocks, being occupied by aqueous solutions, serve the purpose of condensers. The conditions are those which would obtain between steam generated in a boiler connected by many openings with condensers containing water. Almost as fast as the steam is developed it is liquefied in the condensers, thus heating the contained water. Thus gaseous solutions are condensed to liquids almost as rapidly as formed. It is possible that in the zone of fracture immediately adjacent to a great mass of intrusive igneous rocks there may be a narrow border area in which the water may be maintained as a gas and rise toward the surface, because it is driven by its expansive force from places of high temperature to places of low temperature, but evidence is necessary upon this point.

In attempting to arrive at the probability of the importance of gaseous solutions in the zone of fracture it is necessary to consider the manner in which igneous rocks solidify. It is well known that in this zone the intrusive igneous rocks ordinarily show sahlbands, giving evidence of quick chilling and solidification along their borders. From the exteriors crystallization extends inward. It is therefore plain that the surface of crystallization is ever a changing one. It should also be remembered that rocks are poor conductors of heat. It has further been pointed out that as crystallization and condensation continue openings are likely to form along the contacts, and thus give ready passages for water. The question is whether in the zone of fracture, along the borders of the intrusive masses, where there is free circulation, the temperature would be long maintained above the critical temperature of water. It seems to me that the probability is strongly against this. This probability is confirmed by observation, which shows that minerals produced along the contacts of igneous rocks in the zone of fracture are those characteristic of the belt of cementation, and therefore the same as those known to be produced by aqueous solutions. There is therefore no good reason for supposing that ores adjacent to the igneous rocks in the belt of cementation are commonly precipitated from

gaseous solutions. But it would not follow that the aqueous solutions precipitating the ores do not receive contributions of gases, water, and metals from the contiguous igneous rock as it crystallizes and continues to cool after crystallization.

CIRCULATION IN ZONE OF ANAMORPHISM.

In the zone of anamorphism the conditions are very different. Here the openings are normally minute and disconnected, although locally and for a brief time of active intrusion they may be large and continuous. The amount of water in the surrounding rocks is very small, and the openings are so minute that it can not make its way readily toward the igneous masses. Consequently there is in this zone no condenser available to transform the gaseous solutions to the liquid condition. The temperature is certainly high, probably often above the critical temperature of water, because of the normal increase of temperature due to depth, and because of the high heat of the igneous rocks. Under these conditions it is natural to suppose that adjacent to the igneous rocks gaseous solutions are produced in considerable quantity, probably largely as emanations from the igneous rocks, but also to an important extent by transformation to the gaseous condition of the free water of the adjacent rocks and of the water liberated by the process of dehydration. Gaseous solutions would utilize the large openings temporarily formed to the fullest possible extent. It has been explained that the gaseous solutions, having very little viscosity and under the great pressure of this zone, make their way through the minute openings of the rocks and even between the individual mineral particles. The gaseous solutions emanating from the igneous rocks and produced from the surrounding rocks may contain metallic material in considerable quantity. Such gaseous solutions from various sources would deposit minerals in the larger openings precisely as do aqueous solutions under similar circumstances. Ores would probably be deposited even more extensively as impregnations in the minute openings of the adjacent rocks. The places where precipitation occurred would be controlled in part by the strength of the rocks, rigid rocks furnishing openings of a larger size than those which are more plastic. The localization would be very largely controlled also by the composition of the rocks. If they were able to take part in a reaction which would result in a precipitation, this would

influence the result. For instance, it will be seen (pp. 1086–1087) that calcium carbonate may be very influential in precipitating the sulphides from aqueous solutions. It is supposed that the same reactions may take place with dense gaseous solutions at high temperatures; indeed, it might be argued that the calcium carbonate would be even more active with gaseous solutions than with aqueous solutions. In this connection the very frequent occurrence of the disseminated ores and deposits with irregular boundaries, with garnet, pyroxene, tourmaline, and other heavy anhydrous minerals as simultaneously developed gangue minerals in limestone is to be noted. (See pp. 1052–1056.)

CIRCULATION OF AQUEOUS SOLUTIONS.

The general circulation of aqueous solutions is a function of the amount of water in the rocks, of the form, continuity, size, and amount of the openings in the rocks and of difference in head, difference in temperature, and mechanical action.

As to the amount of water in openings, in some cases the openings are not full and in some they are full, or the rock is saturated. Where the rocks are not saturated the chief forces producing circulation are gravity and molecular attraction. Gravity tends always to carry the water downward. Molecular attraction, or what is ordinarily called capillarity, tends to draw the water to places where the pore spaces have little water. It therefore is an effective force only where the rocks are not saturated with water. In the saturated rocks the forces producing movement are gravity, heat, and mechanical action. Where the rocks are saturated hydrostatic pressure is active, and therefore under these conditions flowage is usually much more rapid than where the rocks are not saturated. The flowage is also rapid in proportion as there is unequal head and unequal temperature in the two columns. The movement of water caused by gravity is due to the unequal weights of the columns of moving water. The unequal weight may be due to difference in the lengths or in the temperatures of the vertical columns or the two combined. That difference in length gives difference in weight is obvious. Where two connected columns of water have unequal temperature, the cooler column is the denser of the two, and therefore under these circumstances gravity in connection with heat produces circulation. In regions where the increment of heat is normal, there may be

movement due to difference in temperature, but probably it is of great consequence only where the heat increment of one column is more than normal on account of mechanical action or of igneous rocks, or both. Mechanical action may squeeze out the water in the openings of rocks or possibly even some of the combined water and thus produce circulation. (See pp. 149, 661–665.)

Where the rocks are saturated, whatever the cause of the flow of underground water, the direction of movement is from places of greater pressure to places of less pressure. A current going in any direction is evidence of an excess of pressure in the rear of the current. Thus, water which enters by seepage or through capillary tubes into a larger opening, such as a fissure, must be under greater pressure than the column of water into which it makes its way. Whether the motive force in the movement of the water be difference in gravitative stress, of deformation, or any other cause, the excess of pressure resulting in movement is behind the current. In proportion as the opening approaches a circular form the flow increases because the friction between the moving water and the film of fixed water upon the walls is less per unit volume. The more continuous the openings, the more rapid is the flowage. Flowage increases as the size of the openings increases. In super-capillary openings the ordinary laws of hydrostatics apply, and therefore the flowage may be very rapid. In capillary openings the laws of capillary flow apply, and the movement of water is slow. Where the openings are subcapillary, the attraction of the mineral particles extends from wall to wall, the water films are glued to the rocks, and flowage is inappreciable. Flowage increases as the amount of openings or the pore space increases.

So much for the laws controlling the general circulation of aqueous solutions. The combinations of the various factors are so fundamentally different in their effects in the zone of fracture and zone of combined fracture and flowage that further statement is necessary in reference to them

CIRCULATION IN ZONE OF FRACTURE, OR ZONE OF KATAMORPHISM.

In the zone of fracture a great many openings are of super-capillary and capillary size, and many of them are continuous. It is clear that in this zone the conditions are very different in the belt of weathering above the level of ground water where the rocks are commonly not saturated and in the belt of cementation below the ground water where the rocks are saturated. Each belt requires consideration.

BELT OF WEATHERING.

The belt of weathering comprises the belt at the surface of the earth in which the rocks are not continuously saturated with water. Its thickness is ordinarily between 0 and 300 meters; it is commonly less than 100 meters, but in the arid regions it may be exceptionally 1,000 meters. In the belt of weathering the openings in rocks are upon the average more numerous, and larger than in any other belt. The amount of water present may vary from a very minute fraction of the amount required to fill the pore spaces to saturation. Therefore there is greater variation in the amount of water in the belt of weathering than in any other belt. The water is derived from rainfall and from the belt of saturation. At a given place, the rainfall varies greatly from time to time and there is much variation in the amount of water. It is shown (see pp. 416–423) that the forces which control the movement of aqueous solutions in this belt are gravity and molecular attraction and that these work directly and also through plant roots and mechanical movements.

So far as ore deposits are concerned, the direct actions only are important. Gravity steadily tends to carry the water downward. Molecular attraction ever tends to carry the water from places of more abundance to places of less abundance. The movements of the water due to these two factors are very complex in the upper portion of the belt of weathering, but for the middle and lower portions the movement of the ground water is mainly controlled by gravity. Therefore in these parts of the belt the water usually steadily descends. In considering ore deposits this is the fundamental point in connection with the belt of weathering, as the lateral movements and the ascending movements are unimportant.

The level of ground water for a given area is not fixed, and in consequence of its variation a certain layer near the boundary between the belt of weathering and the belt of cementation, may alternately be in one belt and in the other. There are various causes for this fluctuation, of which changes in amount of rainfall, orogenic movements, and denudation are important. Where uplift and denudation are the rule, the belt of weathering migrates steadily downward and consequently encroaches on the belt of cementation. Where there is subsidence and valley filling it is not uncommon for the belt of weathering to be encroached upon by the belt of cementation. These transfers from one belt to another will be seen to be of considerable importance in the genesis of ore deposits.

BELT OF CEMENTATION.

The belt of cementation is the belt between the bottom of the belt of weathering and the top of the zone of flowage. Since in places the rocks are saturated to the surface of the ground, and since in the strongest rocks the depth of the zone of flowage under the most favorable conditions may reach 10,000 to 12,000 meters, the possible maximum thickness of the belt of cementation is 10,000 to 12,000 meters. The average thickness of the belt of cementation is probably less than 5,000 meters. Since the temperature increases 1° C. for 30 meters, the water in the lower part of the belt of cementation is above the boiling point for atmospheric pressure. Indeed, if the belt of cementation extends to a depth of 10,950 meters, the water at this rate of increase would have a temperature of 365°, or the critical temperature of water. But it has been shown (pp. 566–569) that, notwithstanding the high temperature of the water up to the critical point, the pressure is sufficient to hold it in the form of a liquid. Where mechanical movements or igneous intrusions have taken place the increase of temperature may be higher than 1° C. for 30 meters. But if the critical temperature be not reached, the increment of temperature must be very much greater than this amount in order that the water shall be changed to the form of a gas. (See pp. 566–569, 659–660.) Igneous intrusions at various times and places have doubtless raised the water above the critical temperature, but such water does not come under the subject now being considered.

The circulation of aqueous solutions in the belt of cementation is vigorous and extensive. The evidence for this is abundant. First, it is known that a considerable percentage of all meteoric water reaches the belt of cementation. All of this water except the inappreciable portion which enters into combination, after a longer or shorter journey in this belt, must somewhere again issue from it, unless a part of it makes its way downward into the zone of anamorphism, and there is no evidence to show that it does this. (See pp. 665–667.) The vigor of the circulation in the belt of cementation is further shown by the almost incredible number of springs carrying a vast volume of water, all of which are supplied by water from this belt. The water issuing from the belt of cementation in springs is probably only a small fraction of that which passes to the overground circulation by seepage through many small widely dispersed openings. (See pp. 413–423, 571–589.)

The strongest evidence of the vigorous and extensive character of the circulation in the belt of cementation is the fact, so strongly emphasized on pages 562–565, that cementation is universal in it. Wherever porous rocks have long remained in the belt of cementation an enormous amount of material has been deposited by underground aqueous solutions. In most cases where the porous rocks have been deeply buried in this belt for geological ages cementation is nearly or quite complete. Thus great sandstone formations have been transformed to quartzite by deposition of interstitial silica. In the San Juan district of Colorado great tuff formations of Tertiary age have been completely cemented. In order to get an idea of the original porosity of this formation it should be compared with the very recent porous cinder cones made up of bombs and lapilli, such as occur at many places in the West, as for instance near Flagstaff, Ariz. These cinder cones are so porous that rain water, however great its amount may be, passes into them as it would into a sieve, and therefore performs no work of erosion. Indeed, it seems as if the process of erosion of such deposits could scarcely begin until the openings had been partly filled by the process of cementation. Yet in the San Juan district of Colorado thousands of meters of tuffs originally as porous as these have been so perfectly cemented that the microscope scarcely discovers an opening except those which have been produced by recent fracture since cementation. The fillings of the major and minor openings are continuous physically and are composed of the same kind of material. No one who has studied such a formation as this can doubt that the general cementation and the filling of the fractures were performed by the same agent.

In general, in the rocks which have been long within the belt of cementation, the innumerable bedding partings, faults, joints, fissility and breccia-tion openings have been closed. The complete cementation of the more porous sandstone and tuffs requires the deposition of mineral material to the extent of 30 to 40 per cent of the volume of the rock. It has been shown (pp. 571–572) that to have accomplished this work the amount of water which circulated through the rocks probably in most cases must have been 100,000 or more times as great as the material deposited. Further, in case of the San Juan tuffs, the enormous amount of water required to deposit the immense mass of cementing material passed through the rocks since early Tertiary time.

Wherever rocks are exposed which once possessed numerous and large openings and which have been in the belt of cementation for a long time, their general cementation gives conclusive evidence of a vigorous past circulation. In consequence of the process itself the openings become smaller and smaller; consequently the circulation less and less vigorous until, when the process of cementation is complete or nearly so, the circulation becomes very feeble. Thus in many regions, humid and arid alike, where there has been vigorous underground circulation, and where great quantities of material have been deposited by the aqueous solutions, the circulation now may be relatively unimportant. At many mining districts these conditions now exist. At the time of rapid deposition of the ores there was a pervasive and vigorous circulation which, as cementation continued, gradually became less and less, and finally practically ceased. But after the ground-water circulation becomes feeble or practically stops, in consequence of cementation, earth movements may again fracture the rocks, and thus a new circulation be inaugurated which results in further cementation and perhaps in further concentration of ore.

In such cases the amount of the present circulation is proportional to the fracturing which has taken place so recently that the openings formed have not had time to be filled again. In contrast with the circulation in formations containing numerous large openings is that in rocks which contain few openings larger than subcapillary size—such as shales and the massive igneous rocks. In rocks such as these, unless orogenic movements produce capillary or super-capillary openings, the circulation may never be vigorous. The existence of impervious formations, either original or produced by the processes of cementation themselves, will be shown later to be very important factors in the general circulation of underground waters and in the localization of ore deposits.

The aqueous circulation of the belt of cementation for homogeneous mediums is fully discussed on pages 571–589. It is there seen that the movement of the water may be resolved into two components—horizontal or lateral movements and vertical movements. In simple cases these components are usually combined in such a way that the lateral component is continuously in the same general direction, and the vertical component of the curved path is first downward and later upward. (See figs. 7 to 11.) But in areas of marked topographic relief a part of the water may

move continuously downward from the place where it enters the rock to where it issues from it. The form of the curved path is influenced by many factors of which the increase in temperature with depth, limiting formations, the preferential use of large channels, the relative lengths of the vertical and horizontal components are the more important.

The greater the temperature the less the viscosity of water. At 90° C. the viscosity is only one-fifth as great as at 0° C., and at 300° C. the viscosity may not be more than one-twentieth of the amount at 0° C. Since the flowage in capillary openings, which is the prevalent abundant kind in rocks, is inversely as the viscosity, the increase of temperature with depth is plainly favorable to deep penetration.

The movement of any aqueous circulation is practically stopped by strata in which all or nearly all of the openings are subcapillary. In the most favorable case for depth this would be the bottom of the zone of fracture. In many cases, however, limiting strata are found at very moderate depths, and there may be several limiting strata bounding pervious strata. (See fig. 12.) In all such cases a given circulation is stopped by the limiting strata, and the lines of flow are thus severely confined. The influence of limiting impervious strata upon the ground-water circulation is well illustrated by many of the artesian systems. Of the various combinations which result in artesian flow a limiting impervious stratum above a pervious stratum is the most common.

In general it may be said for a system of circulation that the entire available cross section is utilized, but not uniformly. Other things being equal, the more direct route is used to a greater extent than a less direct one, and therefore the remoter corners of a water system may have relatively small circulations.

Since the vertical movement of ground water is at a maximum confined to the zone of fracture, it can not exceed 10,000 or 12,000 meters, and commonly is much less than this. Indeed, in many systems of circulation the greater part of the water does not reach a depth as great as 1,000 meters.

There is no assignable limit to the extent of the lateral movement, but commonly it is longer than the vertical movement, in many cases hundreds or thousands of times longer. For instance, in the artesian circulation of the Dakota sandstone the horizontal journey of the water is at least from the

Black Hills to the James River Valley, about 400 kilometers, whereas the vertical circulation is limited to a depth less than 1,000 meters. In this case the vertical journey is insignificant in magnitude as compared with the horizontal journey. While this is an extreme case, in general the horizontal journey is several to many times longer than the vertical journey.

Large channels are utilized to a much greater extent than small channels. This preference for large channels frequently amounts to dominance, particularly for the latter part of the journey. Large channels may be called the trunk channels of circulation. The importance of trunk channels is due to the fact that (1) large channels are likely to be more direct than smaller channels, and (2) the friction along the walls per unit of water is very much less than in capillary and in subcapillary channels. In the belt of cementation, as a rule the channels are larger and more numerous in its upper part, and steadily diminish in number and in size with depth. Therefore large channels tend to produce a shallow circulation, and thus counteract the influence of lessened viscosity with depth and the effect of gravity, which tends to produce a deep circulation. (See pp. 578–582.) The preferential use of trunk-channels leads to the conclusion that fault, joint, and bedding-parting openings, and those of conglomerates, all of which are likely to be of supercapillary size, are largely utilized by the ground-water circulation.

As a matter of observation, it is well known that the water which joins the belt of cementation is distributed throughout the belt, and that it enters at an infinite number of points. It is further known that at least a large part of the water issuing from the belt of cementation emerges from trunk channels. Combining these facts with the principles controlling the circulation, it follows that the circulation of the belt of cementation is analogous to that of a tree, the twigs and branches of which have an important downward component, the medium branches of which are approximately horizontal, and the trunk channel of which usually has an upward component.

CIRCULATION IN ZONE OF COMBINED FRACTURE AND FLOWAGE.

Circulation in the zone of combined fracture and flowage is intermediate in its nature between that of the zone of fracture and the zone of flowage. It has been pointed out (pp. 766–768) that as the bottom of the zone of fracture is approached probably the openings decrease in size, until

they approach those of subcapillary size which are characteristic of the zone of flowage. But because of variations in the nature of the rocks this change does not take place uniformly, but irregularly. Hence one would expect that in formations where the deformation is mainly by fracture the movement of the water would be similar to that of the zone of fracture, but less vigorous, and that where the deformation is mainly by flowage the movement of the water would be unimportant.

CIRCULATION IN ZONE OF FLOWAGE, OR ZONE OF ANAMORPHISM.

In the zone of flowage, which corresponds to the zone of anamorphism, the circulation of water is very different from that in the belt of cementation. While much of the water in the upper parts of this zone is probably liquid, in the deeper parts of it, and in those parts where recent orogenic movements or great batholithic intrusions have occurred the solutions probably reach a temperature higher than 365°, and therefore are in the gaseous condition.

The openings of the zone of anamorphism are for the most part subcapillary and discontinuous. They are not only small in size, but small in total volume. In the zone of anamorphism, therefore, the quantity of free water at any one time is very small as compared with the zone of fracture. So far as the solutions in the zone of anamorphism are aqueous they are mainly glued to the walls of the subcapillary openings, and the circulation under conditions of quiescence is extremely slow. If there were no additions to the free water, doubtless the circulation would be unimportant so far as ores are concerned. But it is shown (pp. 662, 679–680) that one of the most characteristic reactions of the metamorphism of this zone is liberation of the combined water by dehydration, thus continually adding to the amount of free water. It is certain that this excess of free water is squeezed out of the zone of anamorphism, and it is shown (pp. 665–667) to be highly probable that the major movement of this liberated water is upward into the zone of fracture rather than downward into the centrosphere. This highly heated water carries with it carbon dioxide liberated by the process of silication and as much mineral material as it is able to transport.

This upward movement may be largely as gaseous rather than as liquid solutions. So far as this is true the laws of these solutions apply rather than those of aqueous solutions.

SOURCE OF THE METALS.

The nature of the rocks which contribute the metallic salts has been much discussed. With Sandberger,[a] I have little doubt that the metallic constituents of ores are in large part derived from the igneous rocks which have been intruded into or extruded upon the lithosphere. In my paper on "Some principles controlling the deposition of ores," as originally published,[b] I strongly advocated the idea that igneous rocks are the direct source of some ores, that they are the ultimate source of all ores, and that the heat of the igneous rocks is of fundamental importance in the segregation of the ores. The igneous rocks as a source of metallic ores are especially important at periods of exceptional volcanism. At such times there rise from the lower parts of the lithosphere, and possibly to some extent from the centrosphere, enormous masses of igneous rocks which are injected into the zone of fracture or brought to the surface. While, during the middle and later portions of geological time the magmas which came into the zone of fracture or were spread over the surface of the earth were derived from unknown depth, it is entirely possible that, during the early stages of the earth's history, magma very generally existed near or at the surface, and that such magma may have furnished a portion of the metals which now occur in ore deposits, although in such cases doubtless the metals have been distributed and redistributed again and again. From the earliest geological time the igneous rocks have been the original source of the sedimentary rocks, although their immediate source may have been other sedimentary rocks. From the sedimentary and igneous rocks metamorphic rocks are produced. Therefore the original source of all ore deposits is believed to be magma.

I have further held that there is every gradation between igneous action and aqueous action, or, as I have stated it "under proper conditions water and liquid rock are miscible in all proportions."[c] I believe that there are complete gradations between purely igneous pegmatitic dikes and purely aqueous vein material. (See pp. 720–728.) Moreover, in previous papers[d]

[a] Sandberger, F., Untersuchungen über Erzgänge, Wiesbaden, 1885, 2d Heft, pp. 159–431.

[b] Trans. Am. Inst. Min. Eng., vol. 30, 1901, pp. 27–177.

[c] Van Hise, C. R., Principles of North American pre-Cambrian geology: Sixteenth Ann. Rept. U. S. Geol. Survey, pt. 1, 1896, p. 687.

[d] Van Hise, C. R., Metamorphism of rocks and rock flowage: Bull. Geol. Soc. Am., vol. 9, 1898, p. 299. Also this monograph, Chapter VII, pp. 566–569; Chapter VIII, pp. 659–660.

and in this monograph I have emphasized the point that if at any time the temperature of the solutions exceed 365° C. they are necessarily gaseous. I have also held that there is every gradation from ore deposits produced by pure magmatic differentiation through those deposited by gaseous solutions to ores produced by the work of underground water at ordinary temperature.[a]

But it has been explained (see pp. 1014–1016) that igneous rocks influence the segregation of ores in other important ways than by contributing the metals, viz, by heating the solutions of the surrounding rocks and furnishing hot solutions to them, by producing channels for circulation, and by furnishing impervious formations so as to converge solutions into trunk channels.

Le Conte pointed out many years ago that the undoubted frequent occurrence of workable ore deposits in regions of volcanism may be explained by the heat furnished by the igneous rocks, thus promoting the work of underground solutions.[b] That the heat furnished by the igneous rocks is a very important factor in the production of the ore deposits, I have no doubt. Since it is often difficult to prove that the metallic content of an igneous rock is original, it is impossible to make any general statement as to whether the metallic content or the heat furnished by the igneous rocks is the more important in the production of the ore deposits. It seems clear to me that both are very important; and equally clear that in many cases both work together. That is to say, an igneous rock may furnish all or a part of the metal which appears in an ore deposit, and the heat of the same igneous rock may greatly assist its concentration by underground waters of meteoric origin.

While the later igneous rocks are the undoubted source of some, perhaps many, ore deposits, it is also equally certain that another large part is derived from the sedimentary rocks and the metamorphosed, or partly metamorphosed, igneous and sedimentary rocks. As a case clearly illustrating the importance of igneous rocks in increasing the activity of solutions and enabling them to derive a large amount of material from the adjacent sedimentary rocks, there may be mentioned the Mammoth Hot

[a] Van Hise, C. R., Some principles controlling the deposition of ores: Am. Inst. Min. Eng., vol. 30, 1901, pp. 174–175.

[b] Le Conte, Jos., On the genesis of metalliferous veins: Am. Jour. Sci., 3d series, vol. 26, 1883, p. 10.

Springs of Yellowstone National Park. At this place there issues a vast amount of water, and great, brilliant travertine deposits, consisting of almost pure calcium carbonate, have been built up.[a] In this vicinity are Tertiary sediments which include limestones. There can be no doubt in this case that the waters are heated by the igneous rocks, and that the source of the material which is dissolved by the heated waters is the intruded sediments and not the igneous rocks. The case is particularly conclusive, because the geyserite deposits in the adjacent basins where sedimentary rocks are not close at hand consist of silica. If the heat of the igneous rocks can be so effective in promoting the solutions of vast quantities of calcium carbonate in the adjacent sedimentary rocks, may it not be equally effective in dissolving a sufficient amount of gold, silver, and copper, so that in a deposit a fraction of an ounce of gold, a few ounces of silver, or a few per cent of copper may be found?

It is also certain that many ore deposits derive their metalliferous content in part from the intrusive and in part from the intruded rocks. Probably this is the most frequent of all cases. To give an estimate of the relative amounts of metalliferous metals derived from the original igneous rocks and from the secondary rocks is quite impossible.

Recently there has been a strong tendency among many geologists to maintain that the metals in ore deposits are mainly or wholly derived from almost immediately adjacent igneous rocks. As already intimated, this is undoubtedly true in many cases. For instance, where there is a great complex of aqueous and igneous rocks of many different kinds and the ores are always intimately associated with one particular kind of igneous rock and no other, it is very probable that the source of the metal is the intimately associated igneous rock. Such cases are rather numerous. An excellent illustration is furnished by the copper-nickel deposits of Sudbury, which are invariably associated with norite. Another case in which it is believed that the ore is mainly derived from the igneous rocks is that of the copper deposits of the Lake Superior region, which occur in amygdaloids and conglomerates, but a portion of the copper was probably leached from the conglomerates. This belief is not based upon the fact that these ores occur to a considerable extent within openings of the amygdaloids,

[a] Hague, Arnold, Weed, W. H., Iddings, J. P., Yellowstone National Park: Geol. Atlas U. S., folio 30, U. S. Geol. Survey, 1896.

for the conglomerate deposits are even more important, but it is based upon the fact that copper, both in the native form and to a less extent as a sulphide, is sparsely disseminated throughout the basic Keweenawan lavas of the entire Lake Superior Basin. This broad relation has much greater significance to me with reference to the source of the metal than does the association of the ore with an igneous deposit at a particular mine.

Spurr notes substantially the same relations between the ore bodies of the Monte Cristo district of Washington and the associated tonalite. He says that metallic sulphides are everywhere noticeable throughout the tonalite; that scarcely a cross fracture occurs through which there has been water circulation and not some concentration of sulphides; and that in the solid tonalite itself there are local segregations of sulphides. Furthermore, he says there are all gradations from these bunches of sulphide in the fractured rocks through a slight dissemination of sulphides to the ore deposits along the major fractures, such as those of the Mystery and Pride mines. Accepting this statement of fact, there is strong warrant for the suggestion of Spurr that the ores are derived "directly by concentration from the tonalite in which they lie."[a]

While in many instances it is therefore believed that a contiguous igneous rock is the main source of the metal for ore bodies, by some this connection is over-emphasized, and the cases in which this is not true are often ignored. Doubtless this is a consequence of the fact that gold and silver are usually in mind when ore deposits are considered. Gold and silver ores may rather frequently be derived largely from recognizable igneous rocks, but to a very large extent, even for gold and silver, the immediate source of the metal in the deposits heretofore exploited was not the original igneous rocks. For instance, placers, which have yielded more gold to the world than any other form of deposit, have derived their metals from veins, from previous placers, and from the widely dispersed gold in many kinds of rocks. Much of the gold of many placers has been worked over by the processes of nature several times.

If we turn to iron, a metal of vastly greater importance than gold and silver combined, in few or no deposits now exploited can the metals be said to be derived directly from igneous rocks. Again, the deposits of lead and

[a] Spurr, J. E., The ore deposits of Monte Cristo, Washington: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, pp. 828–829.

zinc of the Mississippi Valley, from which 90 per cent of the zinc and more than 20 per cent of the lead of the United States are mined, have certainly not derived their metals directly from igneous rocks. It is rather probable that the metals for these deposits, originally in rocks of unknown origin, have been taken into solution in the belt of weathering, have been transported to the sea, and there precipitated in minute quantities at the time the magnesian limestone formations of the Mississippi Valley were built up. The immediate source of the metals for the present deposits is agreed by all who have closely studied them to be the Cambro-Silurian limestones.

The conclusion is reached that these rocks are really the source of the lead and zinc, because almost everywhere through the great Cambro-Silurian limestones small amounts of these metals are found. In cracks and crevices at innumerable localities there are very minor segregations of galena and blende, but not in sufficient amount to constitute ore deposits. Furthermore, Robertson has made analyses of the fresh solid Cambro-Silurian limestone where it showed no galena or blende to the eye, and very small amounts of lead and zinc were found.[a]

Thus the reasons leading to the conclusion that the Cambro-Silurian limestone is the source of the lead and zinc ores of the Mississippi Valley are precisely the same as those leading to the conclusion that the Keweenawan lava is the main source of the copper deposits of the Lake Superior region.

If these ore deposits in limestones are derived from the sediments, why should it be assumed, in cases of ore deposits in sedimentary rocks, especially in limestones cut by igneous rocks—as in the copper districts of Arizona and New Mexico, in the Leadville, Tenmile, and Aspen districts of Colorado, in the Mercur district of Utah, in very many other places in the United States, and at a greater number in other parts of the world—that the associated igneous rocks, frequently subordinate in volume, constitute the sole source of the metals lead, copper, gold, zinc, and iron?

The foregoing facts show that the source of the metal for an individual district is not to be ascribed a priori to igneous, sedimentary, or metamorphic rocks, but can be determined only after an inductive investigation of the facts. The metal of a district may be derived from the late igneous

[a] Winslow, Arthur, Lead and zinc of Missouri: Missouri Geol. Survey, vol. 7, 1894, p. 480.

rocks, from ancient igneous rocks, from sediments, from metamorphosed rocks, or from any combination of the above. When the important economic districts of the world are inductively studied, and certain knowledge obtained, I believe that it will be discovered that a great number, if not the majority, of ore deposits are not the result of a single segregation, but are the accumulated fruits of a great interrupted process of segregation, a part of the metals for the deposits having been worked over many times by the metamorphic processes.

According to this view, it has been shown in Chapter XI, on the redistribution of the elements, that a general result of metamorphism and accompanying processes is that many of the secondary rocks are depleted in reference to each metal, and that correlative with such depletion other deposits are formed in which each metal is segregated. Since these processes result in deposits in which each of the common metals is segregated, why should we hold that the metal of a present deposit of gold or silver or copper is derived solely from an immediately adjacent igneous rock unless evidence for this be conclusive? The natural view is that the metallic ore deposits of the world are, broadly, the accumulated results of the processes of segregation carried on throughout geological time.

While it is held that the metals for very numerous and important ore deposits do not have their immediate source in igneous rocks, it is recognized, as stated at the outset, that ultimately the metals for all ore deposits are probably to be traced back to igneous rocks. Since leaving their original positions the metals for many ore deposits have been transferred and segregated here and there until they reached the places where they are now found.

It is recognized that this general statement as to the sources of metals for ore deposits will be unsatisfactory to many persons, as every one is more or less influenced in his view by his own personal experience and by the particular metals which he has studied, but it is not the purpose of this chapter to consider individual districts, except as they illustrate principles. It is properly the part of the geologist or mining engineer who studies an individual district to find the source of the metals. In many cases careful investigations can undoubtedly determine this point, as, for instance, in the Lake Superior iron region. In other districts, however, the most exhaustive

study may not enable the investigator to determine the source of the metals. This is especially likely to be true of ore deposits produced by ascending waters from a somewhat deep circulation. The underground waters may have their sources of supply in rocks which do not reach the surface, and have not been penetrated by the mine workings.

In concluding this part of the subject it may be suggested that in many instances mistakes have been made in assuming that some one formation, sedimentary or igneous, is the sole source of the valuable metals. Such an assumption is particularly prevalent in papers descriptive of gold and silver deposits. In many districts where there are a number of sedimentary and igneous rocks I have no doubt that the silver and gold are partly derived from two or several formations.

PART II. SEGREGATION OF ORES.

GENERAL STATEMENTS.

We are now prepared to consider each of the divisions of ores. It will be seen that the different divisions, groups, classes, and subclasses of ores are based upon the last dominant genetic process concerned in their production. It has just been explained that there has been a steady redistribution of the metals, each of them being taken away from some of the formations, and, corresponding with this, segregated elsewhere. Looked at from this point of view, an existing ore deposit may represent the result of segregations by many processes throughout geological time. Thus, if the full history of a metal in a given ore deposit were known it might be found that at different times parts of it had been segregated by various sedimentary, igneous, and metamorphic processes. Not only is this so, but the segregations by these various processes may have occurred and recurred. It is therefore manifestly impossible to give the full history of ores, or to apply a genetic classification to them which does not restrict itself to the later dominant processes which resulted in the segregation of the ores at the particular places where they now are. Even thus restricted it will be found that some ore deposits placed in one division or class could, with almost equal plausibility, be placed in another.

DIVISION A. ORES PRODUCED BY PROCESSES OF SEDIMENTATION.

Since ores produced by processes of sedimentation do not properly fall within the scope of a treatise on metamorphism, they will be considered only to the extent necessary to show their relation to the division of ores somewhat fully discussed—that produced by processes of metamorphism.

The ores produced by processes of sedimentation may be divided into two groups—those formed by chemical precipitation, and those formed by mechanical concentration.

ORES FORMED BY CHEMICAL PRECIPITATION.

Ores produced by chemical precipitation comprise some of the iron, manganese, and aluminum deposits.

Bog deposits of iron ore, of recent origin and doubtless in some cases within older rocks, are the direct results of chemical precipitation. The processes by which these develop—the leaching of the metal from the land areas, and its transportation and precipitation as limonite in shallow bodies of water—have all been fully treated in connection with the development of iron carbonate and limonite (see pp. 824–829, 842–845), therefore the process will not be here again described. Some manganese deposits are, in part at least, the direct result of chemical precipitation, the lines of development being the same as those of limonite.

Hayes holds that certain bauxite deposits also are the result of chemical precipitation. According to his views the aluminum for some of the bauxite deposits of Arkansas was taken into solution by underground water, was brought to the surface by springs which issued into a shallow sea, where the aluminum and iron oxides were chemically precipitated. (See Chapter XI, p. 985.) Since these deposits are considered in the chapter on the redistribution of the elements nothing further will be said here in reference to them.

Aluminum and iron are the most abundant of the metals, while manganese is rather plentiful. Again the law of mass action applies. The abundant metals are those which are likely to be thrown down as chemical sediments in sufficient amount to constitute ore deposits.

ORES FORMED BY MECHANICAL CONCENTRATION.

Mechanical concentrates may be divided into residual deposits, stream deposits, and beach deposits. The term placer, originally used for stream deposits, has been, in some cases, extended to seabeach deposits.[a] The principles which result in the production of residual deposits, stream deposits, and seabeach deposits are the same.

The valuable materials segregated have a high specific gravity and are relatively indestructible. In consequence of their capacity to resist mechanical wear and chemical solution they are segregated in alluvial deposits, in the sands and gravels of streams, and on beaches of lakes and oceans, because the other constituents are transported, worn, or dissolved more readily than is the resistant valuable product. In the production of residual deposits the capacity of the valuable material to resist solution is of dominating importance, and in the production of beach and stream deposits the valuable material must have power to resist both solution and wear.

The ores produced by mechanical concentration comprise both metals and oxides. The important metals belonging to this group are gold, platinum, iridium, and osmium. Practically all of the last three metals which have been exploited have been derived from placers. But of the metals produced by processes of sedimentation gold is the one of dominating importance. To the end of the nineteenth century a very large fraction of all the gold extracted from the earth by man was derived from placers.

The oxides which occur as mechanical concentrates are those of tin (cassiterite) and iron (magnetite). For the first of these compounds the placer deposits are of great importance, but for the iron oxides are relatively unimportant. Although much cassiterite has been taken from veins, for many years the chief supplies of tin ore have come from the East Indies—the so-called Straits tin—and all except a relatively insignificant amount of this cassiterite has been derived from mechanical concentrates.[b] The Malay Peninsula now produces almost 50 per cent of the tin of the world;

[a] Schrader, F. C., and Brooks, A. H., Some notes on the Nome gold region of Alaska: Trans. Am. Inst. Min. Eng., vol. 30, 1901, pp. 236–247.

[b] Rolker, C. M., The production of tin in various parts of the world: Sixteenth Ann. Rept. U. S. Geol. Survey, pt. 3, 1895, pp. 458–492.

the adjacent islands, Banca and Billiton, produce about 25 per cent. Doubtless this tin is of the same origin as that of the Malay Peninsula. Thus it appears probable that substantially 75 per cent of the tin of the world is derived from mechanical concentrates.[a]

In a small way magnetite beach sands have been utilized. Those of New Zealand are best known.[b]

An excellent illustration of an iron-ore deposit produced by mechanical concentration was that of Iron Mountain, Missouri, where considerable masses consisting of well-rounded bowlders of hematite[c] were found scattered over the mountain as a residual deposit and buried in pre-Cambrian ravines under Cambrian and Silurian deposits.

METAMORPHIC ALTERATIONS OF SEDIMENTARY ORES.

No sooner are ore deposits produced by processes of sedimentation than they are subject to the metamorphic processes, and thus are modified to a variable extent. Sedimentary deposits, whether originally formed in the belt of weathering or in the belt of cementation, later may be in the belt of weathering, in the belt of cementation, in the zone of anamorphism, or partly in one and partly in another. In each case the deposit is subject to the metamorphic processes of the horizon in which it may be. Where a deposit is in the belt of weathering, the material may be dissolved to some extent and the metal carried downward into the belt of cementation. If a deposit is in the belt of cementation valuable minerals may be added to or taken away from it as a consequence of the work of underground water. If the material is partly in the belt of weathering and partly in the belt of cementation a portion of the material dissolved in the belt of weathering may be carried downward and deposited in the belt of cementation, and thus the lower part of the deposit enriched at the expense of the upper part. If the material reaches the zone of anamorphism it may there undergo the alterations of that zone. After having been subject to the metamorphic effect of a certain belt or zone a deposit may be transferred to another belt or zone and thus the alterations of this zone be

[a] Penrose, R. A. F., jr., The tin deposits of the Malay Peninsula, with special reference to the Kinta district: Jour. Geol., vol. 11, 1903, pp. 135–154.

[b] Birkinbine, John, The production of iron ores in various parts of the world: Sixteenth Ann. Rept. U. S. Geol. Survey, pt. 3, pp. 29–186, 186.

[c] Nason, F. L., Iron ores of Missouri: Geol. Survey Missouri, vol. 11, 1892, pp. 27–3

superimposed upon the previous alterations. These later alterations by metamorphism, like the earlier ones, may greatly diminish or greatly increase the value of the original sedimentary deposit. In consequence of the varying action of the secondary metamorphic processes an ore deposit may be chiefly due to the direct processes of sedimentation or chiefly due to metamorphic processes. There are therefore all gradations between deposits produced solely by the processes of sedimentation and those formed entirely by the processes of metamorphism.

This is especially well illustrated by the gold placers. Many of these deposits are in large part in the belt of weathering, but extend downward into the belt of cementation. It has been repeatedly explained that in the belt of weathering ferric and cupric sulphates and chlorides are produced. These are capable of dissolving gold. Doubtless other solutions are formed which have similar power. Wherever these solutions traverse placers it is little short of certain that the gold is dissolved to some extent. The material may be dissolved in the belt of weathering, transported downward to the belt of cementation, and there precipitated; and thus one part of the deposit may be enriched at the expense of another; or solution may take place throughout a deposit and, in consequence, a placer be impoverished; but the abstracted material may be precipitated in another deposit, so that correlative with the depletion of some deposits there may be enrichment of others.

The formation of placer deposits has not been restricted to the present geological period. It is highly probable that throughout geological time placer deposits of greater or less richness have been produced, although it is likely that those in early geological times were comparatively small. In many cases as denudation continues the material of placers is largely transported to the sea, and so forms beach deposits. It at first might be thought surprising that so few ancient beach deposits of gold have been found, but this is partly explained by the fact that gold is undoubtedly dissolved in sea water, since the ocean contains compounds capable of dissolving this metal. When the gold is transported to the seabeach, it is in a very favorable position to be finely ground by attrition, and in this fine condition is especially subject to the solvent action of the sulphates and chlorides of the sea. It has been estimated that in sea water there is a greater amount of gold than has been extracted from the earth by man.

While some of this gold was undoubtedly transferred to the sea in solution by the streams, it is believed to be probable that a major part of it was transferred to the sea by the streams mechanically, and by the action of the sea upon the beach deposits the gold was dissolved.

River deposits and beach deposits may in consequence of physical changes be buried under later deposits, and thus pass far down into the belt of cementation or even into the zone of anamorphism. They are then subject to all the metamorphosing processes of the belts in which they occur. In the belt of cementation the circulating underground water will superimpose its work. As illustrating this principle may be mentioned the difference of opinion which exists as to the great gold deposits of the Rand. These deposits, according to Becker, are dominantly marine beach deposits,[a] although he agrees that the gold has been rearranged to some extent by underground water,[b] thus explaining the crystallized character of portions of the gold and the existence of gold in cracks within the quartz pebbles.[c] But Becker holds that not more than a minute fraction of 1 per cent of the gold has been introduced from an extraneous source. Others have held that the Rand deposits are of alluvial origin, i. e., stream placers; and still others believe that the gold was deposited from solution at the time the gravels accumulated.[d] Upon the other hand, Curtis[e] and Hammond[f] both insist that all of the gold was deposited by underground water, and therefore the deposits belong to the class produced by processes of metamorphism.

Recently an excellent statement of facts in reference to these deposits has been made by de Launay.[g] According to this author the gold exists in pyrite contained in the siliceous cement, together with other metamorphic minerals, such as chlorite and muscovite. Much of the pyrite is rounded like rolled grains, but a larger part is well crystallized and presents sharp angles. De Launay is unable to decide between the hypotheses (1) of

[a] Becker, Geo. F., The Witwatersrand banket, with notes on other gold-bearing pudding stones: Eighteenth Ann. Rept. U. S. Geol. Survey, pt. 5, 1897, pp. 160–177.

[b] Becker, cit., p. 171.

[c] Becker, cit., p. 176.

[d] Becker, cit., pp. 169–170.

[e] Curtis, J. S., The banket deposits of the Witwatersrand: Eng. and Min. Jour., vol. 49, 1890, pp. 200–201.

[f] Hammond, John Hays, Gold mining in the Transvaal, South Africa: Trans. Am. Inst. Min. Eng., vol. 31, 1902, pp. 841–845.

[g] De Launay, L., Observations on the Rand conglomerate: Eng. and Min. Jour., vol. 75, No. 14, 1903, pp. 519–521.

placer deposits, (2) of simultaneous chemical precipitation with mechanical accumulation of the gravel, and (3) of introduction of the gold into the conglomerate by underground waters since its formation. He rejects the idea of a combination of these, saying that "this would only uselessly complicate the hypothesis." It seems to me that the only hypothesis which explains the facts is a combination of the placer and metamorphic processes.

Where two men differ so radically as do Becker and Hammond, the truth may lie between, as is so often the case. Each is possibly partly right and partly wrong. It is natural to think that a given ore deposit can not be produced partly by the processes of sedimentation and partly by underground water. These two classes of deposits are automatically assumed not to grade into each other, whereas it is perfectly clear that such gradation may and probably does exist. It may therefore be suggested that a closer study of the Rand deposits will show that they are partly in the nature of mechanical sediments and partly in the nature of deposits segregated by underground water. If this be the fact, study should be directed to determine the quantitative importance of each.

The placers of California and New Zealand furnish an instance in which it is certain that both mechanical concentration and later chemical modification by underground water have played a part.[a] In these placer deposits, and especially in the deep placers, crystallized gold occurs not infrequently, and it must be held that at least the rearrangement of this gold has been due to the work of the underground water since the formation of the placers. If this be admitted, the question at once arises as to what extent gold has been added by the circulating waters since the placers were formed. The added gold may have been derived from the leaner upper portion of the placers, from the surrounding rocks, including the veins, or in part from both sources.

It is clear from the foregoing that mechanical concentration or secondary metamorphic action may be the dominant factor in producing a sufficient amount of segregation to make an ore deposit, or both may be necessary in order to accomplish this work.

The chemical and mechanical ore deposits particularly well illustrate the principle that ores can be classified only upon the basis of the last

[a] Gordon, H. A., Hysteromorphous auriferous deposits of the Tertiary and Cretaceous periods in New Zealand: Trans. Am. Inst. Min. Eng., vol. 25, 1896, pp. 292–301.

process which is concerned in their segregation. Almost any one of these deposits illustrates the idea. For instance, a sedimentary deposit of bog iron or manganese is finally concentrated by precipitation of these materials in a marsh or lagoon. But the earlier stages of the work of segregation are by underground water, and if this part of the work were considered the ores would be classified as metamorphic. Again, the mechanical concentrates are not mainly segregated from the sparsely dispersed metal in the original rocks, but are segregated from previous segregations, which may be the result of igneous, sedimentary, or metamorphic processes, or some combination of the two or three. To illustrate, the gold placers of the Sierra Nevada chiefly derived their gold from the vein deposits of the same mountain system. The segregation of the gold within these veins is the most important part of the process and it will be considered under the work of underground water, but the last process—mechanical concentration—produced the placers and it must be taken as the basis of classification. Similar statements could be made with reference to the residual cassiterite of the Malay Peninsula or the residual iron ore of Iron Mountain, Missouri.

DIVISION B. ORES PRODUCED BY IGNEOUS PROCESSES.

Ores produced by igneous processes, like those produced by processes of sedimentation, do not properly come within the scope of this treatise upon metamorphism. They will, therefore, be considered only so far as necessary to show their relation to the ores produced by processes of metamorphism.

Ores directly produced by igneous processes are regarded as a small division by those who have most closely studied them. The recent advocates for a direct igneous origin for certain ore deposits include Vogt, Beck, Kemp, Spurr, and others. Emmons[a] has also favored the idea of at least a first concentration of the metallic contents of ores by processes of differentiation of igneous rocks, more particularly the basic rocks. Spurr has recently well summarized the principles which result in the segregation of ores by magmatic processes.[b]

[a] Emmons, S. F., Geological distribution of the useful metals in the United States: Trans. Am. Inst. Min. Eng., vol. 22, 1894, pp. 53–95. The mines of Custer County, Colo.: Seventeenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1896, pp. 470–472.

[b] Spurr, J. E., A consideration of igneous rocks and their segregation and differentiation as related to the occurrences of ores: Trans. Am. Inst. Min. Eng., vol. 33, 1903, pp. 288–341.

Since upon the whole Vogt has most closely studied ores produced by magmatic segregation, and has been the most vigorous advocate for the existence of such, I quote from him a paragraph giving a list of deposits which he believes to be of igneous origin:

> Ore deposits formed by simple magmatic differentiation are confessedly infrequent, and therefore relatively subordinate in importance to other classes. Under this head may be named: (1) The occurrences of titanic iron ores in basic and intermediate eruptives, perhaps also of iron ores in acid eruptives; (2) those of chromite in peridotites and their secondary serpentines (and also according to J. H. Pratt, those of corundum in the peridotites of North Carolina); (3) a number of deposits of sulphide ores, particularly the nickeliferous pyrrhotites occurring in gabbro (at Sudbury, Canada, Lancaster Gap, Pennsylvania, many places in Norway and Sweden, and Varallo, in Piedmont); (4) according to some authorities, the auriferous pyrites of Rossland, British Columbia; (5) according to B. Lotti, the high-grade copper ores occurring in serpentinized peridotites in Tuscany and Liguria, Northern Italy (for instance at Monte Catini), and analogous occurrences in other regions; (6) the occurrences of metallic nickel-iron (without economic value) in eruptive rocks; (7) those of the platinum metals in highly basic eruptive rocks, etc.
>
> It may be pretty safely assumed that the foregoing list will be enlarged by future investigations, though it can never become very extensive.[a]

Of these classes the first mentioned, the titanic iron ores, is probably the largest. This class of ore deposits has been elaborately considered by Vogt, and a full list of illustrative localities is given by him.[b] Of such ore deposits the only ones with which I am familiar are the titaniferous magnetites at the base of the Duluth gabbro in the Lake Superior region. While I have not studied these deposits closely I have no reason to dissent from Vogt's belief that they are differentiation products of the gabbro magma. Recently Lindgren has described a very large titanic iron ore deposit at Iron Mountain, Wyoming, which I understand him to believe to be derived by magmatic segregation from an igneous rock.[c] The total mass of titaniferous iron ores is large, but much of this material is of low grade. It is for the most part high in titanium, averaging about 12 to 20 per cent of titanium oxide, but occasionally having as little as 3 per cent.[d]

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[a] Vogt, J. H. L., Problems in the geology of ore deposits: Genesis of ore deposits, 2d ed., published by Am. Inst. Min. Eng. 1902, pp. 642–643.

[b] Vogt, J. H. L., Weitere Untersuchungen über die Ausscheidungen von Titaneisenerzen in basischen Eruptivgesteinen: Zeit. für prak. Geol., Jahrgang 1900, pp. 233–242, 370–382; Jahrgang 1901, pp. 9–19, 180–186, 289–296, 327–340.

[c] Lindgren, Waldemar, A deposit of titanic iron ore in Wyoming [a paper presented to the Geological Society of Washington]: Science, new ser., vol. 16, 1902, pp. 984–985.

[d] Kemp, J. F., Titaniferous iron ores of the Adirondacks: Nineteenth Ann. Rept. U. S. Geol. Survey, pt. 3, 1899, pp. 387–388.

In consequence of their low grade and the difficulty of smelting them, titanium ores are at present of little or no economic importance. In the future, when high-grade nontitaniferous ores are exhausted, or nearly exhausted, it is possible that such ores will be an important future resource for iron.

In connection with iron ores produced by magmatic segregation the question naturally arises as to why they are titaniferous. The answer is substantially that they are titaniferous because they are magmatic segregations. The magnetite in diabase, gabbro, and other basic rocks is almost universally titaniferous. This being true, it naturally follows that where this magnetite is segregated in sufficient quantity to be an ore such ore is titaniferous.

So far as I know, all of the iron ores which have been shown to be magmatic segregations are titaniferous. The majority of the great iron-ore deposits which are at present worked are known to have been produced by the action of aqueous solutions. (See pp. 1193–1197.) In view of this fact and the history of titaniferous magnetites, it seems to me highly probable that none of the nontitaniferous ores of iron are magmatic segregations.

Certain corundum deposits are the result of direct igneous processes. For instance, the corundum syenite of eastern Ontario, Canada, is to all appearances, as shown by its textures and structures, a coarse igneous rock.[a] Apparently the magma was so very aluminous that at the time of crystallization not all of the alumina was able to combine with the various acids, and hence a part of it separated as an oxide, or corundum, precisely as iron oxide, which does not unite with the acids.

As to the production of titanic magnetite and corundum ores by magmatic processes there is no difference of opinion. But it appears to me that a point which should be emphasized in this connection is that aluminum and iron are the two most abundant metals of nature, and therefore they are the ones which are most likely during crystallization of magmas to segregate as oxides to such an extent as to produce ores.

The extent to which magmatic segregation must take place in order to produce an igneous ore of iron or aluminum is comparatively small. To illustrate, the average amount of metallic iron in original igneous rocks is 4.64 per cent,[b] and in the basic rocks in which magmatic iron ores occur it

[a] Miller, W. G., Economic geology of eastern Ontario; corundum and other minerals: Rept. Bureau of Mines, vol. 7, pt. 3, 1898, pp. 210–213.

[b] Clarke, F. W., Analyses of rocks, laboratory of the U. S. Geol. Survey, 1880–1899: Bull. U. S. Geol. Survey No. 168, 1900, p. 15.

is more than this, being 8.66 per cent in the Duluth gabbro of Minnesota.[a] Therefore to produce an ore-body by magmatic segregation in such a rock as this the iron need be increased only about seven times. The production of ores of the less common metals by direct magmatic segregation is an entirely different matter. In the original igneous rocks the amounts of copper, nickel, cobalt, gold, silver, etc., are usually so small as not to be detected by assay. In order to produce ores of these metals segregation must take place many fold, probably in all cases more than a hundredfold, and in many cases probably a thousand or many thousand fold. Those who maintain that an ore deposit of any of these less common metals is produced wholly by magmatic segregation should determine the ratios between the amount of metal in the original igneous rock and in the ore, and show that the igneous processes have segregated the metal to that extent.

These considerations apply to the other cases of ore deposits held by Vogt to be due to magmatic segregation and to the gold-ore deposits referred by Spurr to the same processes. Thus to segregate chromite from peridotite and the sulphides of the less common metals from igneous rocks by magmatic processes alone would require an amount of segregation which is yet to be proved. Of the sulphides ores that of nickel is the one which has most strenuously been held to be due to magmatic segregation. Of nickeliferous pyrrhotites, I have seen deposits at only one locality, near Sudbury, Canada, where they are associated with norite. I shall not deny that a first segregation of these deposits along the border of the norites may have taken place in part as a consequence of magmatic differentiation. Walker[b] states that in certain cases near the center of the norite masses there is comparatively little pyrrhotite, and that in passing toward the borders the amount steadily increases until the ore deposits are reached. But so far as I have seen the deposits there is a great difference between the nickeliferous norite and the deposits which are mined, a difference between a comparatively small and a high percentage of sulphide. It is these high-grade products which I hold were certainly to a large extent precipitated from circulating solutions. The increase in the amount

[a] Winchell, A. N., Gabbroid rocks of Minnesota: Am. Geol., vol. 26, 1900, p. 374.

[b] Walker, T. L., Geological and petrographical studies of the Sudbury nickel district, Canada: Quart. Jour. Geol. Soc. London, vol. 53, 1897, p. 52.

of sulphide in passing from the center to the border of a norite area is just what one would expect, even if the material had been segregated by circulating solutions, since the trunk channels for circulation are frequently along the borders of intrusive masses, and at such places solutions from the igneous and adjacent rocks extensively mingle. At Sudbury almost conclusive evidence of segregations by solutions is furnished by distinct veins of pure sulphides, evidently formed in openings in the norite. Both walls of some of the veins are impregnated with ore in varying degrees. The impregnation is greatest at the walls, and in passing from them the amount of sulphide gradually lessens until none is visible.[a] In short, the phenomena are absolutely identical with those which Lindgren has described as especially characteristic of metasomatic processes along the walls of fissure veins.

It may be suspected that a close study of some of the other nickeliferous deposits will show somewhat similar phenomena. To what extent circulating underground solutions have concentrated the nickeliferous deposits of Norway and of Varallo in Piedmont I do not venture to say. Nor do I express any opinion as to the part which magmatic segregation has played in the production of the auriferous pyrites of Rossland, British Columbia, and the high-grade copper ores described by Lotti; but Lindgren, as the result of careful studies by himself and previous studies by King and Raymond, states that the Rossland deposits are metasomatic replacements rather than magmatic differentiations.[b] It is to be noted that the copper ores described by Lotti and that chromite ores described by Pratt[c] are in serpentinized peridotites.

In those cases in which the ores are in much altered rocks the question certainly should be asked as to what extent the ores have been modified by the processes of alteration. In the other cases, in which no evidence of secondary action is mentioned by Vogt, it certainly is a proper subject of

[a] While this volume is going through the press a paper by Dickson on the ore deposits of Sudbury has appeared (Ore deposits of Sudbury, by Charles W. Dickson: Trans. Am. Inst. Min. Eng., vol. 34), which gives a full summary of the views that others have held in reference to the genesis of the Sudbury ores and contains an elaborate discussion of the facts of occurrence of these ores. As a consequence of his elaborate study, Dickson concludes that "while magmatic differentiation has gone on to some extent, the *sulphides are not the result of it.*" He says further: "It might be safely stated that at present the whole weight of the evidence points to the secondary formation of the Sudbury ore bodies as replacements along crushed and faulted zones, with only minor indications of open cavities."

[b] Genesis of ore-deposits: Am. Inst. Min. Eng., 2d ed., 1902, pp. 564–565.

[c] Pratt, J. H., Occurrence, origin, and composition of chromite: Trans. Am. Inst. Min. Eng., vol. 29, 1900, pp. 22–24.

inquiry as to what extent magmatic segregation has produced the deposits and to what extent subsequent metamorphic action has been influential. I suspect it will be ascertained, as is so frequently true of ore deposits, that in some of the cases cited the ores, instead of being due to a single process at one period, are due to a combination of processes. Even if a first segregation were made by direct igneous action, as maintained by Vogt, such deposits may have been further enriched by metamorphic processes after the first concentration. (See pp. 1235–1236.)

Concerning the occurrence of metallic nickel-iron in eruptive rocks, and platinum in highly basic rocks, it may be merely remarked that such deposits are not ores. It is well known that not only these, but various other metals, such as copper, occur widely distributed in igneous rocks, and, indeed, it has been shown that in such rocks, directly or indirectly, all ores have their ultimate source. But before the term "ore" can be properly applied to such rocks it should be shown that there is at least a reasonable chance that the economic conditions will be such that some metal may sometime be exploited with profit. It follows that the occurrence of sparsely disseminated metals of various kinds through igneous rocks has no bearing upon the question of the segregation of ores by igneous processes alone.

Spurr, holding that pyrrotite veins are due to magmatic segregation, has applied the same explanation to the gold-quartz veins of the Yukon.[a] He says the pure quartz veins are produced at the final stage of crystallization in connection with igneous rocks when the residue "is little more than hot siliceous water, which contains, besides silica, small quantities of many other rock elements which have not been taken up by the rock-forming minerals."[b] Later, but with no further field study or additional evidence, Spurr goes somewhat further in his views toward magmatic segregation. Explaining the origin of the Yukon and other gold-bearing quartz veins, he says:

> Therefore it has been concluded that certain quartz veins in the Yukon district (part, at least, of which are auriferous) have originated by a process of magmatic segregation, which has separated them from other materials while in the state of aqueo-igneous fusion (the condition of molten rock in general), and that they represent the siliceous extreme of that process. From this standpoint, they are a variety of the igneous rocks. But it has been shown that as magmas become more siliceous

[a] Spurr, J. E., Geology of the Yukon gold district, Alaska: Eighteenth Ann. Rept. U. S. Geol. Survey, pt. 3, 1898, pp. 311–316.

[b] Spurr, cit., p. 312.

they also contain more water; so, when the stage of quartz veins is reached, the magma is believed to be so attenuated that it may best be described as water highly heated and heavily charged with mineral matter in solution.[a]

He further states that there is no great difference between veins originating in this manner and those having other origins. On this point he says: "A quartz vein originating by magmatic segregation often might not be distinguishable from one formed in the many other ways which are possible."[b] The only difference which he suggests between gold-quartz veins of magmatic origin and those deposited by aqueous solutions is that the gold ores supposed to be produced by magmatic segregations are "without the admixture of so great proportions of the commoner metals as is usual in ore deposits."[b] Spurr, however, gives no reasons showing the applicability of this criterion. From my own point of view, I should regard it as applying in the reverse direction. That is to say, if the exceedingly rare metal, gold, be segregated by magmatic processes to such an amazing extent as to produce an ore deposit, it seems to me to be exceedingly likely that other metals would be segregated in connection with the gold ores so as to be present in greater amounts than usual.

Since Spurr gives no certain criteria by which gold-quartz veins supposed to be produced by magmatic segregation are to be discriminated from those formed by solutions, I take the conservative view that gold-quartz veins have their origin in solutions, and I ask for positive evidence from those who assert that such quartz veins are produced by magmatic segregation alone.

In general, concerning the production of ores of the metals other than those of iron and aluminum by magmatic segregation alone, I repeat that it seems to me that the enormous amount of segregation required should be taken into account, and that it should be most conclusively shown that this process alone produces the ores before the conclusion be accepted that during the crystallization of the magma segregation took place to the necessary extent.

While Vogt,[c] Beck,[d] Lindgren,[e] and others believe in a direct igneous

[a] Spurr, J. E., A consideration of igneous rocks and their segregation or differentiation as related to the occurrence of ores: Trans. Am. Inst. Min. Eng., vol. 33, 1903, p. 311.

[b] Spurr, cit., p. 311.

[c] Vogt, J. H. L., Problems in the geology of ore deposits: Trans. Am. Inst. Min. Eng., vol. 31, 1902, pp. 131–147.

[d] Beck, R., Lehre von der Erzlagerstätten, Berlin, 1901, pp. 700.

[e] Lindgren, Waldemar, Character and genesis of certain contact deposits: Trans. Am. Inst. Min. Eng., vol. 31, 1902, pp. 242–244.

origin of certain ore deposits, they hold that far more numerous and important ore deposits[a] are of contact-metamorphic origin instead of the result of direct igneous action. This view is an old one supported by von Cotta,[b] von Groddeck,[c] de Launay,[d] and many others. Still others have used the word "contact after-action" apparently as marking a grade of deposit between contact metamorphic deposits and deposits laid down by aqueous solutions.

Lindgren, considering the phenomena of pegmatitization under the principle already mentioned, that liquid rock and water are miscible in all proportions, has suggested a relation between pegmatite veins and ore deposits; but he is careful to say that the relation between the pegmatites and quartz veins must be proved, and that this has not yet been done. He further says that the California, Idaho, and Oregon gold-quartz veins show no relation whatever to pegmatitic dikes. He also calls attention to the auriferous quartz veins of North Carolina, described by Pratt, which occur together with barren lenses of pegmatitic quartz.[e]

Thus Lindgren, who has studied the gold-quartz veins of the United States more extensively than any other geologist, recognizes the fact that so far as his observations go the productive auriferous gold-quartz veins, even if associated with and possibly dependent upon pegmatitic action, are not the deposits which have ordinarily been referred to as pegmatites. Although strongly holding that the majority of fissure veins are "genetically connected with bodies of intrusive rocks,"[f] Lindgren states that in those great fissure veins which he has studied in the West he has not been able as yet to identify the igneous rocks with which the veins are connected genetically. Further, he says that the waters which deposited gangue minerals of the gold-quartz veins and gold "are chiefly surface waters, which, after a circuitous underground route, have found in a fissure an easy path on which to return."[g]

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[a] Vogt, J. H. L., Problems in the geology of ore deposits: Trans. Am. Inst. Min. Eng., vol. 31, 1902, pp. 137–140.

[b] Cotta, B. von, Erzlagerstätten im Banat und in Serbien, Wien, 1864.

[c] Groddeck, A. von, Die Lehre von den Lagerstätten der Erze, Leipzig, 1879, p. 260.

[d] Launay, L. de, Traité des gîtes minèraux et métallifères, Paris, vol. 2, 1893, pp. 245–258.

[e] Lindgren, Waldemar, Character and genesis of certain contact deposits: Trans. Am. Inst. Min. Eng., vol. 31, 1902, pp. 243–244.

[f] Lindgren, Waldemar, Metasomatic processes in fissure veins: Trans. Am. Inst. Min. Eng., vol. 30, 1901, p. 691.

[g] Lindgren, cit., p. 691.

Vogt, although so strong an advocate for igneous action, does not include among ore deposits formed by eruptive after-action in connection with pegmatite veins any gold, silver, copper, lead, zinc, or iron deposits. There is therefore agreement between Vogt, Lindgren, and myself upon the fundamental point that the great class of ore deposits which have been known as contact metamorphic deposits were deposited by underground solutions. There is also agreement that the igneous rocks in various instances constituted the partial or chief source from which the metals are derived. There is further agreement that the waters which deposited the materials were hot, and derived their heat largely from the igneous rocks. It follows from this that we agree that the ores were mainly put into their present places during the time in which the igneous rocks were able to produce a contact effect through hot solutions. There is also agreement that the water depositing the ores was derived from two sources, the ordinary circulating underground waters and water derived from the crystallization of the magmas themselves. So far as the waters were derived from the latter source, it is further agreed that in many cases they were rich in metalliferous material, and therefore unusually effective. Probably in some cases solutions from the igneous rock were more important than those of the meteoric origin.

In a genetic classification of ores upon the basis of agency there is no place for the contact deposits. It does not follow that no ore deposits are produced in connection with contact metamorphism. Contact metamorphic ores must be produced by direct magmatic processes and therefore be igneous ore deposits, by gaseous solutions, by aqueous solutions, or by some combination of the three. In other words, the terms contact metamorphism and eruptive after-action are too vague to give any precise meaning with reference to the deposition of ores. That this is so is shown by the very different usages of the words "contact metamorphism" and "eruptive after-action" by different authors. It is perfectly clear that different deposits, or even the same deposit, produced in connection with contact metamorphism or eruptive after-action may belong partly to igneous ores, gaseous ores, and aqueous ores. Shortly after intrusion there may be magmatic segregation along the border of the igneous rocks; later, in the process of cooling, additions may be made to the ore deposits by gaseous

solutions; and still later, when the rocks have further cooled, further additions may be made by aqueous solutions. Indeed, I suspect that a considerable number of ores have had such a composite history, viz, first, segregation by magmatic processes, further segregations by gaseous solutions, and finally segregations by aqueous solutions. I hold this latter stage to be commonly the one in which occurs the final concentration necessary to make a deposit of value, and therefore entitled to the name of ore. In the field the general terms "contact-action," to cover all of these three kinds of work, and "contact metamorphic ores," to cover the total result, may be useful; but one can not make a classification of ore deposits in which he introduces at the same time contact metamorphic ores and the classes of igneous ores, gaseous solution ores, and aqueous solution ores.

DIVISION C. ORES PRODUCED BY PROCESSES OF METAMORPHISM.

It is believed that ore deposits produced by processes of metamorphism are of dominant importance. While ore deposits produced by processes of sedimentation and by igneous processes are of great consequence, they together are subordinate in importance to those produced by processes of metamorphism.

Ores produced by processes of metamorphism may theoretically be divided into two groups—those deposited in their present positions by gaseous solutions and those deposited in their present positions by aqueous solutions.

The second group is believed to be more important than all other ore deposits. I hold, therefore, that the dominant agents which deposited ores in their present positions are aqueous solutions. How important is the group of ores deposited by gaseous solutions is uncertain, as the criteria have not been fully worked out by which these deposits can certainly be discriminated from those precipitated from aqueous solutions.

GROUP A. ORES DEPOSITED BY GASEOUS SOLUTIONS.

Ores deposited from gaseous solutions comprise all those ores which are precipitated from gaseous mixtures of all kinds. They therefore include all deposits actually formed by pneumatolytic, fumarolic, and solfataric action. That ore deposits have been precipitated from gaseous solutions

has been a favorite hypothesis ever since ores were a serious subject for investigation. The idea goes back as far as Élie de Beaumont,[a] who supposed that the majority of ore deposits were thus produced. This theory has been especially applied to ores of mercury and tin. During the last ten years the idea has again been taken up and emphasized by a considerable number of vigorous advocates, of whom Vogt, Beck, Lindgren, Weed, and Kemp are well known.

Recently Weed[b] gave a classification of ores in which he separates pneumatolytic deposits, fumarolic deposits, and gas-aqueous deposits, giving each as one of the major classes. The deposits here placed by Weed together comprise a very large proportion of ore deposits. Spurr[b] also has given a classification of ore deposits in which contact metamorphic deposits, deep-seated gaseous deposits, fumarolic deposits, and solfataric deposits are recognized as classes. Weed divides his pneumatolytic, fumarolic, and gas-aqueous deposits into subclasses and groups. Moreover, the ores of gold, silver, and copper of many well-known districts are assigned to each of these classes and to the various subdivisions of the classes. However, neither Weed nor Spurr gives the criteria by which he distributes the various ores among the pneumatolytic, fumarolic, solfataric, and gas-aqueous deposits. Nor are the criteria even given by which deposits are known to be formed by gaseous solutions. It has been shown that the heavy anhydrous minerals of the zone of anamorphism probably develop at temperatures above that of the critical temperature of water. (See pp. 182–185, 685.) This has led me to hold that where such minerals have developed with ores formed from solutions, such solutions are gaseous. But I am unable to formulate any criteria, except purely theoretical ones, which subdivide the deposits of gaseous solutions into pneumatolytic, fumarolic, and solfataric. Indeed, I hold that the entire class of ore deposits produced by gaseous solutions, while important, is small as compared with ores deposited from aqueous solutions.

Ores deposited from gaseous solutions above the critical temperature of water may conceivably be produced in the zone of anamorphism in con-

[a] Bull. Soc. géol. de France, 2d ser., vol. 4, 1846–47, p. 1249.

[b] The genetic classification of ore bodies, a proposal and a discussion (including papers by W. H. Weed and J. E. Spurr): Eng. and Min. Jour., vol. 75, 1903, pp. 256–258.

sequence of the normal increase of temperature with depth. But probably ore deposits belonging here are more commonly produced in connection with eruptive rocks or orogenic movements, or both; that is to say, the eruptive rocks and earth movements are important factors in raising the water above its critical temperature. It has already been seen that ores may grade from those deposited by igneous agencies to those deposited by aqueous agencies. At one end the ores are the result of magmatic processes; at the other end the ores are deposited by water. At an intermediate stage it is to be supposed that ores may be deposited from gaseous solutions above the critical temperature of water, viz, 365°.

Lindgren says: "We may assume with great confidence that at the contacts of intrusive rocks with a sedimentary series the temperature usually exceeded 365° C., and the pressure 200 atmospheres."[a] Theoretically one would expect that rather frequently in connection with great intrusive masses, and especially in connection with batholitic masses, the water in the surrounding rocks would be raised above its critical temperature, and therefore that its action is pneumatolytic. But the practical question is concerning the importance of gaseous solutions in connection with the ores. What are the ores which were thus deposited? What are the criteria by which they may be identified? The only metallic deposits which Vogt regards as produced by eruptive after-action in the sense of pneumatolytic action, are cassiterite veins.[b] Beck agrees in regarding the tin deposits of Zinnwald, in Saxony, as due to pneumatolytic action.[c]

While it may be possible that some tin deposits may be produced by magmatic segregation or pneumatolytic action, it by no means follows that all of the tin or even a greater part of it is of this origin. Recently Penrose has visited and studied the deposits of the Malay Peninsula.[d] Here, as is well known, the greater portion of the tin is actually obtained from the alluvium; but Penrose's studies have shown that the tin of the alluvium has its original source in veins in the granite axis of the peninsula and in the limestones flanking this axis. The ore in these rocks is associated with sulphides, such as bornite and chalcocite, and occurs in veins which have

[a] Lindgren, Character and genesis of certain contact deposits, Trans. Am. Inst. Min. Eng., vol. 31, p. 238.

[b] Vogt, cit., pp. 132–137.

[c] The origin of ore deposits (discussion by R. Beck): Trans. Am. Inst. Min. Eng., vol. 31, 1902, p. 945.

[d] Penrose, jr., R. A. F., The tin deposits of the Malay Peninsula, with special reference to those of the Kinta district: Jour. Geol., vol. 11, 1903, pp. 135-154.

all the characters of ordinary water-deposited veins, and which are substantially alike both in the granite and in the limestones. Were it not for the cassiterite there would be no reason to suggest that these deposits differ in any way from other vein deposits produced by underground water. (See pp. 1058–1065.) As already pointed out, about 75 per cent of the tin of the world is produced in the Malay Peninsula and from Banca and Billiton. The product is mainly a mechanical concentrate, but the cassiterite for this concentrate is derived from the veins in the limestone and granite. Therefore probably 75 per cent of the present product of tin was deposited from aqueous solutions.

Lindgren finds from his study of metasomatic processes in fissure veins that topaz, garnet, tourmaline, and biotite occur as important metasomatic minerals in connection with certain ore deposits. But the metasomatic minerals which are found in an overwhelming preponderance in ore deposits are those which are produced by water action in the belt of cementation, viz., hydrous silicates, carbonates, oxides, etc.

The metallic ore deposits which contain anhydrous minerals Lindgren divides into three classes, (1) topaz-cassiterite veins, (2) tourmalinic gold-copper veins, and (3) biotitic gold-copper veins.[a] Lindgren's description of these veins shows that usually they are not in the igneous rocks, but are largely replacement deposits in adjacent rocks. Pyrrhotite and chalcopyrite carrying gold are found as replacement products in feldspar, and by gradual extension of the processes finally replace the whole rock. The process of formation of the biotitic gold-copper veins is "more characteristic of dynamic metamorphism than of ordinary fissure veins."[b] Lindgren describes the ores between Signal Peak and Meadow Lake as consisting of pyrite, pyrrhotite, and sphalerite, with some galena, with a gangue consisting of quartz, epidote, and tourmaline, with some mica. He says "the ores occur intimately intergrown with this gangue."[c] Lindgren divides the copper deposits of the gold belt of the Blue Mountains of Oregon into various "types." The Seven Devils type, he says, is a contact deposit of chalcopyrite and bornite between limestone and diorite, which has a gangue of garnet, epidote, and other contact minerals. The tourmaline type has

[a] Lindgren, Waldemar, Metasomatic processes in fissure veins: Trans. Am. Inst. Min. Eng., vol. 30, 1901, pp. 619–645.

[b] Lindgren, cit., p. 645.

[c] Lindgren, Waldemar, The auriferous veins of Meadow Lake, California: Am. Jour. Sci., 3d series, vol. 46, 1893, p. 205.

an ore consisting of chalcopyrite and pyrite associated with the gangue of quartz and tourmaline. He here places the Copperopolis mine and Jessie vein. The ores are intergrown with quartz and tourmaline. At the Jessie vein the other gangue materials are calcite, dolomite, and specularite.[a] Lindgren says the copper deposits of the Seven Devils and tourmaline types "are of rare occurrence."[b]

In the South Mountain district of Idaho, an argentiferous galena, with some zinc blende and copper minerals, occurs in crystalline limestone and in schist. The gangue minerals are quartz, calcite, actinolite, brown garnet, and ilvaite, the gangue minerals and ores being intergrown.[c]

Weed states that the Jimenez copper deposits of Mexico follow a line of contact between limestone and granite, the limestone being largely converted into massive garnet.[d] He further states that the Porvenir gold-copper vein in the Sierra Azul mining district of Mexico occurs in granite, and has tourmaline as an abundant gangue mineral.[e]

Yung and McCaffery describe the copper deposits of San Pedro, in New Mexico, as contact deposits in limestone. The limestone has been largely replaced by garnet. Chalcopyrite is intimately associated with the garnet, and with subordinate amounts of specular hematite, epidote, vesuvianite, wollastonite, quartz, and calcite. They say "the ore is always accompanied by garnet, although the garnet does not in all places carry ore. When the garnet carries the ore the chalcopyrite is disseminated throughout its mass, and appears to be of synchronous origin."[f]

In those instances in which it is clearly shown that heavy anhydrous minerals, such as topaz, tourmaline, garnet, and biotite, develop simultaneously with the deposition of the ores by metamorphic processes, it seems highly probable that they formed under the conditions of the zone of anamorphism and that the temperature at the time of the deposition was above the critical temperature of water.

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[a] Lindgren, Waldemar, The gold belt of the Blue Mountains of Oregon: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, pp. 629–630.

[b] Loc. cit., p. 629.

[c] Lindgren, Waldemar, The gold and silver veins of Silver City, De Lamar, and other mining districts in Idaho: Twentieth Ann. Rept. U. S. Geol. Survey, pt. 3, 1900, p. 189.

[d] Weed, Walter Harvey, Notes on certain mines in the States of Chihuahua, Sinaloa, and Sonora, Mexico: Trans. Am. Inst. Min. Eng., vol. 32, 1902, p. 404.

[e] Loc cit., p. 440.

[f] Yung, Morrison B., and McCaffery, Richard S., The ore deposits of the San Pedro district, New Mexico: Trans. Am. Inst. Min. Eng., vol. 33, 1903, p. 355.

In this connection it may be recalled that beautiful crystals of the variety of garnet known as spessartite, fayalite, and topaz occur in lithophysæ in recent volcanic rocks, especially in the openings in them. The formation of these openings in the lavas and the development in them of these minerals naturally suggest the action of gaseous solutions. It has also been pointed out (p. 685) that so far as the heavy anhydrous minerals have been reproduced artificially under conditions where water is present high temperature and pressure have been necessary. For instance, Chrustschoff obtained from water solutions heated to a temperature of 550° C. amphibole, pyroxene, quartz, and adularia.[a]

It thus appears that both observation and experiment strongly favor the idea that such minerals as topaz, garnet, and amphibole, so far as separated from solutions, are deposited by gaseous solutions above the critical temperature of water. If this be so, it follows that those sulphides which were deposited simultaneously with the development of the heavy anhydrous minerals were precipitated from gaseous solutions.

It is evident that it is difficult to make a certain case in favor of gaseous solutions. It must be shown, where the ores occur in connection with the heavy minerals supposed to be formed under conditions of gaseous solutions, that the metals have not been introduced at a subsequent stage when aqueous solutions were the active agent. There should be excluded also the possibility that the ores were deposited by aqueous solutions in the belt of cementation and were later transferred to the zone of anamorphism, where the heavy minerals developed by later alterations in that zone. Apparently in some of the cases above cited the latter possibility is excluded, as all the evidence seems to be in favor of denudation since deposition rather than deeper burial.

Under normal conditions it might be supposed that ore deposits would be produced by gaseous solutions in the deep-seated zone above the critical temperature of water; that above this zone in the belt of cementation ores would be deposited by aqueous solutions, and that above the level of ground water other ore deposits would be produced in the belt of weathering by gaseous solutions. The latter ores would be those to which the terms fumarolic and solfataric are naturally applicable; but, so far as I know, the actual development of ore deposits by gaseous solutions above the

[a] Chrustschoff, K. von, Ueber künstliche Hornblende: Neues Jahrb., 1891, Bd. II, pp. 86–90.

level of ground water is only a hypothesis. If such deposits exist, I know of no criteria which have been worked out by which they may be discriminated from deposits of aqueous solutions.

The hypothesis that the vapors of the metals rise with the vapors of water from an unknown source and deposit ore in the openings of the rocks is exceedingly attractive, but it has been seen that where openings occur in rocks below the level of ground water, the rocks are saturated with aqueous solutions, therefore the locus of the deposition of ores from vapors would be in the belt of weathering. The view that fumarolic and solfataric vapors have deposited ores has been especially prevalent in reference to cinnabar and such easily sublimed deposits. Daubrée has maintained that tin ores are formed by the sublimation of stannic chloride and stannic fluoride and their reaction upon water.[a] For the production of any ore deposit by sublimation in this sense I know no scrap of evidence.[b] In Chapter VI, on "The belt of weathering," it has been seen that where there is fumarolic or solfataric action the rocks are rapidly carbonated, hydrated, and oxidized, the mechanical result being softening and disintegration. The products are colored yellow or brown by oxide of iron. That metallic ore deposits have been produced in connection with such action remains to be proved.

It has already been seen that in various recent classifications of ore deposits, which are made mainly upon the basis of agent, there are also introduced contact action and eruptive after-action. In so far as deposits are precipitated from gaseous solutions, whether the solutions be derived partly from the intruded and partly from the intrusive rock, or partly from both, they belong in this class rather than in an independent class erected on an entirely different basis and therefore an incongruous element in a scientific classification.

GROUP B. ORES DEPOSITED BY AQUEOUS SOLUTIONS.

It has been stated that ores deposited by aqueous solutions are believed to be more important than all others combined. The evidence in favor of this view will not be presented in detail, but a few of the more salient points bearing upon it will be summarized.

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[a] Daubrée, A., Memoir sur le gisement, la constitution, et l'origine des amas de minerai d'étain: Ann. des Mines, 3d series, vol. 20, 1841, p. 65.

[b] This statement is restricted to the metallic ore deposits; it does not apply to deposits of sulphur and similar compounds made in connection with volcanic action, in reference to which I express no opinion.

First, it has been shown (pp. 571–572, 612–640) that the general cementation of the belt so named is due to the work of underground water. The evidence upon this point is briefly summarized in this chapter. (See pp. 1024–1028.) If general cementation is correctly attributed to deposition by underground water, it can hardly be doubted that many ore deposits are due to the same agency, since in general the majority of ore deposits differ in no essential respect from the ordinary cementation products, except that they contain an unusual amount of certain metals of importance to man. If underground water carried and deposited the material in the openings of sand, transforming them to sandstones and quartzites, in the larger openings of conglomerates and great tuff formations, thus indurating them, and in the innumerable openings produced by joint, fault, bedding parting, and brecciation fractures, it follows that similar deposits containing a minute fraction of a per cent of gold or silver, a small amount of copper, or a large quantity of iron—in other words, ores—are also the results of aqueous deposition. However, evidence that the majority of ores are deposited by underground waters does not rest alone upon the general argument of cementation.

The second argument in favor of the deposition of the majority of ores by aqueous solution is the nature of the accompanying gangue minerals and their relations to the ores. The gangue minerals which accompany the great majority of veins are the hydrous silicates, including kaolinite, sericite, the zeolites, and chlorites; the carbonates, such as calcite, dolomite, and siderite; and the oxides, such as quartz and hematite. In other words, the dominant gangue minerals are the identical ones produced on an extensive scale by metasomatic processes within the belt of cementation, and deposited upon a grand scale in the openings of that belt, thus cementing the rocks.

But the conclusion that such minerals are deposited from aqueous solutions does not depend upon their likeness to the minerals of the belt of cementation. Actual observations show that these minerals are now being deposited by aqueous solutions. This has been observed at various places. In this country the most famous localities are Sulphur Bank, California, Steamboat Springs, Nevada, and the Yellowstone Park. Perhaps the best-studied instance of all is that of Boulder Hot Springs, Montana, where the vein deposits and the alterations of the accompanying rock have been recently very closely examined and well described by

Weed.[a] The spring issues through a granite. This granite has been extensively altered into sericite, kaolinite, and zeolite. The filling of the vein consists of quartz, zeolite, and calcite. Weed finds that the vein filling contains a very small amount of gold and silver, and also that the altered granite contains a smaller amount of silver and a trace of gold. The thin sections show the presence of pyrite and hematite. Thus there is actual mineralization of this vein.[b] Substantially the same phenomena as those at Boulder Hot Springs have been long known to exist at Steamboat Springs and Sulphur Bank. It is therefore certain that at those localities, where ore material is accompanied by the minerals characteristic of secondary action in the belt of cementation, the ores were deposited by aqueous solutions. If this be so, it is little short of a certainty that in general the ores associated with similar gangue minerals in the belt of cementation are deposited from aqueous solutions. At any rate, one who maintains that ores so intimately associated with the minerals mentioned as to show contemporaneous deposition are not deposited by aqueous solutions must furnish evidence upon which he reaches a conclusion adverse to all observed facts.

It is to be observed that this reasoning is in accord with the fundamental hypothesis of geology mentioned at the outset of this treatise, viz, that when a certain set of complex forces and agents is observed to produce complex phenomena, and no other combination of forces and agents has been observed to cause such phenomena, the conclusion is that the phenomena are to be referred to the forces and agents now at work.

A third argument showing the direct connection between the recognized work of underground water and deposits of ores has been fully stated by Posepny. For the banded structure so characteristic of fillings of openings in rocks, whether these contain metals in sufficient quantity to be recognized as ores or not, Posepny proposes the term crustification.[c] That crustified or banded or comb veins are usually precipitates from underground waters no one doubts. It has yet to be shown that regular crustification, so general a phenomenon in ore deposits, is produced by any other agent than aqueous solutions.

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[a] Weed, Walter Harvey, Mineral vein formation at Boulder Hot Springs, Montana: Twenty-first Ann. Rept. U. S. Geol. Survey, pt. 2, 1900, pp. 227–255.

[b] Weed, cit., pp. 248–249.

[c] Posepny, F., Genesis of ore deposits: Am. Inst. Min. Eng., 2d ed., 1902, p. 12.

As further evidence of the deposition of ores from aqueous solutions we may now pass to illustrations of ore deposits that exhibit phenomena identical with those which are known to be produced as a consequence of the action of aqueous solutions.

Upon the point that the iron ores are dominantly produced by the circulation of ordinary meteoric waters, there is no difference of opinion; there is general agreement also that these waters are mostly descending waters at ordinary temperatures. (See pp. 1193–1197.) The importance of waters of meteoric origin at ordinary temperatures in the genesis of ores should perhaps be emphasized. Probably the iron ores preponderate in volume over all other metallic ores. In the United States, Great Britain, and Germany 66,000,000 tons of iron ore were mined in the year 1902. It is not probable that this amount is approached by the remaining metallic ores. Not only do the iron ores occur in largest quantity, but iron is a metal of dominant importance. There is no question that the world could spare all the other metals better than it could spare iron. If it be agreed that iron is more important to the advancement of the race than all other metals, and that iron ore occurs in greater quantity than all other ores and is dominantly deposited by meteoric waters at ordinary temperatures, it follows, disregarding the manner of the deposition of any other metals, that the work of meteoric waters at ordinary temperatures is the most important factor in metallic ore deposition.

Other metals also are dominantly deposited by aqueous solutions. Many ore deposits are so associated with the general process and the belt of cementation that one must hold that the work of cementation and the deposition of ores were simultaneously caused by the same agent. For instance, the San Juan tuff of Colorado, a Tertiary volcanic formation, at the time of its deposition must have been exceedingly porous. It is now so thoroughly cemented by quartz and other gangue minerals that the microscope can discover no openings. In the cementation of this tuff formation an immeasurably greater quantity of material was deposited between the fragments than is now found in the veins. The filling of the intersecting veins contains the same gangue minerals as those which cement the tuffs. It is perfectly clear that the formation of these veins was an incident in the general process of cementation. In some of the veins, and to a variable extent in the same vein, a sufficient amount of mineral was

deposited to make the material an ore. The gangue of such veins, the barren veins, and the cement of the tuff are connected physically and are similar mineralogically. Thus it is certain that they are the result of like processes, and few can doubt that the general cement and vein filling were deposited through aqueous solution.

The conglomerates and amygdaloids of Lake Superior furnish conclusive evidence that the deposition of the copper was a mere incident in the general process of cementation. Throughout the Lake Superior region the Keweenawan amygdaloids, sandstones, and conglomerates have been cemented by the minerals which developed in the belt of cementation. Throughout this region, coincident with this process, there was deposited sparsely disseminated copper. Scarcely a Keweenawan district has been studied in which such disseminated copper, associated with the cementation minerals, may not be seen, and in many cases it is sufficiently abundant to warrant exploration with the hope of finding ore deposits. In only a single district, however, that of Keweenaw Point, has copper been discovered in sufficient quantity in veins, amygdaloids, and conglomerates to constitute ore deposits. In every respect these copper deposits are like the remaining great volume of the Keweenawan greenstones, sandstones, and conglomerates, being cemented in substantially the same manner and with the same minerals. At various places on Keweenaw Point from 1 to 4 per cent of metallic copper was deposited simultaneously with the other cementing minerals. There can be no escape from the conclusion that the general cementation of the Keweenawan rocks and the deposition of the copper were performed by the same agent and at the same time. I do not know that any one has ever held that this general cementation is the result of other than aqueous solutions. If this general belief be true it is conclusively shown that the copper was also deposited by aqueous solutions. Other districts similar to those mentioned could be cited.

Passing to veins of lead, zinc, gold, and silver it is found that all but a comparatively small number of such veins exhibit the cementation minerals which have been mentioned. The ores are so intimately associated with these gangue minerals that they must have been simultaneously deposited. In many cases it can be shown that the filling of the veins was contemporaneous with extensive alterations of the walls within which developed like minerals, and with the general cementation of the belt of cementation.

Generalizing in reference to districts, it may be said that, excluding sedimentary deposits, probably all of the great mining camps of the world show the phenomena which indicate deposition by aqueous solutions. Certainly this is true for America. The ore deposits which have been shown to be formed by gaseous solutions, or by magmatic segregation, are at comparatively small and little known camps.

Objection has been raised to the above general statements as to the importance of aqueous solutions, on the ground that in many ore-bearing districts there is not now a vigorous aqueous underground circulation.[a] This may be true of deposits either in humid or in arid regions. Many important humid districts could be mentioned in which the circulation is at present very feeble. For instance, in the deep copper deposits of the Lake Superior region there is little water. The same is true of the San Juan districts of Colorado, of the deep mines of Przibram, and of many other places in the world. Another instance in which deep workings have shown very little circulating water is that of the Newhouse tunnel, at Idaho Springs, Colo. This tunnel, more than 4,000 meters long, in a granite-gneiss-schist complex of rocks, shows but an insignificant amount of water. A small amount percolates in at different places, but the quantity is so small that it is ignored in the drifting arrangements. For arid regions with small circulation the copper mines of New Mexico and Arizona furnish admirable illustrations. Indeed it not infrequently happens that in such regions, after one reaches a moderate depth, the levels are dry, or even dusty.

But from the above facts it is a mistake to infer that when the ores were deposited there was not a vigorous circulation. As has been so fully explained in various places, the very process of cementation lessens the size and number of the openings, and when the process nears completion the openings all become subcapillary and circulation practically ceases. We have already seen that such are the facts in reference to the Lake Superior conglomerates, the San Juan tuffs, and to the rocks of various other regions. The original openings, and the deformation cracks and crevices have been so thoroughly cemented, and since that time so few new fractures have been formed, that but little water can find access from the surface.

[a] Kemp, J. F., The rôle of the igneous rocks in the formation of veins: Trans. Am. Inst. Min. Eng., vol. 31, 1902, pp. 184–198. Rickard, T. A., Water in veins, a theory: Eng. and Min. Jour., vol. 75, 1903, pp. 402–403.

Under present conditions mines may be dry even when the openings have not been closed by cementation. For example, very recently in New Mexico and Arizona there have been important climatic changes. It is well known that these districts were humid in the Quaternary period, during at least two different epochs. During these times the level of underground water was probably as near the surface as it is in the humid districts of the west at the present time. Therefore in these districts in late geological time there was a vigorous underground circulation at those places where cementation was not complete.

The dryness of mines which at the time of the vein filling had a vigorous circulation may be due either to cessation of circulation by cementation or to cessation of circulation in arid regions in consequence of change from humid to arid conditions.

It seems to me that where the gangue minerals are those known to be deposited by aqueous solutions, and the relations of the vein fillings are such as to show that they were deposited contemporaneously with the general cementation material, these facts are decisively in favor of action of aqueous solutions notwithstanding absence of vigorous circulation at the present time. Those who argue that the ores were not deposited by aqueous solutions because there is not now a vigorous aqueous circulation have equally good or better ground for stating that the ores were not deposited by gaseous solutions; for certainly in regions of ore deposits where there is not now a vigorous aqueous circulation there is still more notably a deficiency in gaseous circulation. By a strange inconsistency some of the men who have held that the main class of ores is not deposited by aqueous solutions, and have used as an argument for this belief the absence of a present vigorous circulation, have jumped to the conclusion that such ores were therefore deposited by gaseous solutions, not taking the trouble to ask whether the same argument applied in this case.

In this connection it is to be recalled that in those cases where actual vein filling is now known to be going on, as at Steamboat Springs, Sulphur Bank, Boulder Hot Springs, and various other localities, there is now a vigorous aqueous circulation. Also in some cases of very recent vein formation, as at the Comstock lode and Cripple Creek, where the openings were not fully closed by cementation, an enormous amount of water is handled in mining. The Portland mine at Cripple Creek, Colo., from 1898

to 1902, pumped between 300 and 900 gallons per minute, with maxima for short periods much higher than this.[a] Could there be more decisive evidence that here the circulation is one of extraordinary vigor?

Therefore, I hold, the fact that in many ore-producing districts there is not now a vigorous circulation is no evidence of the nonexistence of such a circulation at the time the deposits were formed.

Finally, while comparatively little stress is to be placed on authority, it is certain that there has been general agreement among the majority of the great workers upon ore deposits as to their deposition by aqueous solutions. Upon this point Bischof, von Groddeck, von Cotta, Daubrée, and Posepny all agree. Posepny differs from some of the authors mentioned in such particulars as the source of the ores and the depth from which the waters rose. Between the authors mentioned there is difference as to whether the waters depositing the ores are mainly ascending or descending, as to the source of the material for deposition, and as to the cause of the circulation of the water. There is no difference between them upon the fundamental point that the great majority of ores are precipitated from aqueous solutions in the positions where they are now found.

My first main conclusion in reference to ores deposited by aqueous solutions is that they form the dominant class.

I. THE SOURCE OF AQUEOUS SOLUTIONS.

Since it has been shown that considerable circulation of underground water in the zone of rock flowage can not be assumed, it follows that we can not suppose that the water of the zone of fracture passes into or is derived from the zone of rock flowage on any large scale. Doubtless this transfer does take place to some extent. Also hydration and dehydration of the rocks are constantly taking place, and these processes at any given place to a small extent subtract water from or add it to the circulation. Further, through volcanism water originally occluded in magma is transferred from the zone of rock flowage, or possibly even from the centrosphere, to the zone of rock fracture, and by the crystallization of the magma is there liberated and thus becomes a part of circulating under-

[a] Ninth Ann. Rept. Portland Gold Mining Co., Pl. XI, 1903.

ground water. But the water of meteoric origin is held to be dominant. It has already been noted that the great iron-ore deposits have been concentrated by waters of meteoric origin. It is further believed that the waters from which were deposited many other ores, the association of which show they were precipitated from aqueous solutions, are also dominantly of meteoric origin. It has been shown already that in order to produce aqueous ore deposits the amount of water required was probably many thousands of times the volume of the minerals deposited. If this be so, even if all the water exuded from magmas at their time of crystallization could be supposed to be converged into the trunk channels holding the ore deposits, this would be but a fraction of that required for the segregation of the ores.

It is impossible to make an exact quantitative estimate of the relative proportions of the waters of meteoric origin and igneous origin concerned in the production of aqueous deposits. But I have no doubt whatever that water of meteoric origin forms more than 95 per cent of such waters, and I think it probable that it constitutes more than 99 per cent, if all ore deposits produced by underground water are taken into account. Mistaken conceptions upon this point frequently have been due to the fact that authors in considering this matter often take into account only ores of a part of the metals, such as those of gold or silver, whereas a general statement with reference to the proportion of water of meteoric origin should take into consideration deposits of iron ore and of the other base metals. Even in the case of ore deposits closely associated with igneous rocks, it is believed that the water is dominantly of meteoric origin. For instance, at the present time, ore deposits are known to be in the course of formation at Steamboat Springs, Sulphur Bank, the Comstock lode and Boulder Hot Springs, Mont., described by Weed.[a] The same is probably also true of the numerous hot springs of Yellowstone Park. The quantity of water which issues from these hot springs is enormous. These springs, in volume of water and in their relation to the topography and precipitation, are in all respects like the vastly more numerous and more important springs which have ordinary temperatures. The study of underground circulation with reference to artesian waters has shown beyond question that the waters discharged from the great majority of springs is of meteoric

[a] Twenty-first Ann. Rept. U. S. Geol. Survey, pt. 2, 1900, p. 227–255.

origin. Numerous large springs are found both in regions in which there has been no igneous action for a long time and in regions in which volcanism is now or has been recently prominent. No one would claim that in regions of the former class the water is of other than meteoric origin. For instance, no one would hold that the waters of the great springs of the Appalachians and the Mississippi Valley are derived from any other source. Why then should this be held in reference to the Cordilleran region of the West? He who maintains that the water for these springs is largely derived from igneous rocks must show that the amount which issues is greater than could be expected upon the meteoric theory, taking into account the precipitation, the climate, the character of the rocks and the topography. The only way to find the effect of an agent, such as igneous rocks, with reference to the water is to compare regions in which these rocks occur with others in which they are absent. Making this comparison, observation has as yet not shown a difference of volume, but in regions of volcanism the waters issuing from springs are frequently hot, and are depositing more than an average amount of mineral material. This difference is therefore logically referred to the igneous rocks. During its underground journey the water comes into contact with or comes near to hot rocks, and thereby becomes heated. In consequence of this it becomes a far more potent chemical agent, and takes into solution a large amount of mineral matter. When gathered into and rising in trunk channels a considerable portion of this mineral matter is deposited. This effect may be accentuated in volcanic regions by mechanical action. As has been pointed out in other places, the deposited material is derived from all the rocks with which the underground water comes into contact during its journey, but in many cases the material is dominantly derived from a single formation or series through which the water journeyed.

While it is held that the water is dominantly of meteoric origin, in regions of volcanism where magmas are crystallizing the heated solutions have doubtless had accretions from this source. But those who hold that the enormous quantities of water issuing from hot springs are mainly derived from crystallizing magmas must furnish the evidence in favor of excepting them from the general rule. The fact that cold springs issue adjacent to hot springs has no bearing on the case, for often trunk channels which issue close together have entirely different feeding areas. Nor is the

fact that hot waters deposit more minerals and different minerals an evidence that the hot waters are derived from crystallizing igneous rocks, although it is possible, and rather probable, that in many instances igneous rocks have contributed materials to the solutions. The high mineral content of waters is adequately explained as a function of high temperature. That this is certainly true for Mammoth Hot Springs has already been shown. (See pp. 1031–1032.) The view that the waters of Boulder Hot Springs and of the Yellowstone Park Springs are of meteoric origin was held by Weed at the time he studied and reported upon these thermal regions.[a]

Adjacent to great intrusive igneous masses the contributions of water from crystallizing magma may be important. Since in many cases the ores are deposited during periods of volcanism, the exuding waters are hot, and may be charged with mineral material to an unusual extent. In such cases the waters derived from igneous sources are proportionately far more active than ordinary underground waters. In many instances the water liberated by the magma during solidification has doubtless acted as a potent agent in segregating the ores, but after solidification waters of meteoric origin continue the work. Often to a large extent the solution of the metal and its deposition takes place after the magma has crystallized, but while the rocks are still hot. After an igneous rock has solidified and continues to cool the ordinary process of shrinkage tends to form openings within it, and especially to form openings along its contact with the contiguous deposits. Orogenic movements also find that the contacts between the igneous and the adjacent rocks are planes of weakness, and are likely there to form openings. This being the fact, it is entirely natural, indeed inevitable, that the hot circulating waters during the time that the rock is cooling are most active in the segregation of the deposits. The extreme activity of hot water in general metamorphism and in the production of ore deposits has been repeatedly emphasized. Thus in various instances the water liberated by the magma at solidification may have played an appreciable part in the segregation of ores, but very often the importance of this part has been overemphasized because it has not been appreciated that after solidification takes place the solutions continue the work of segregation of the ores under most favorable circumstances.

[a] Weed, Walter Harvey, Mineral vein formation at Boulder Hot Springs, Mont.: Twenty-first Ann. Rept. U. S. Geol. Survey, pt. 2, 1900, pp. 249–252.

Summarizing, the conclusion is reached that so far as the main work of aqueous ore deposition is concerned the water is that of meteoric origin, which makes its way from the surface into the ground, there performs its work, and issues to the surface again. The amount of water coming from the deep-seated zone of rock flowage, emanating from crystallizing lava and contributed by dehydration, is believed to be relatively small upon the average, although exceptionally important in proportion to its mass. It is held that, at any given time, the meteoric water entering the crust substantially balances that issuing from it, although there may be a slight continuous surplus in favor of the latter.

My second main conclusion concerning ores deposited by aqueous solutions is that the major part of the water performing the work is meteoric.

II. SOURCE OF METALS FOR ORES DEPOSITED FROM AQUEOUS SOLUTIONS.

It is believed that the greater part of the metals for ores deposited by water is derived from the zone of fracture. If the reasoning thus far be correct, viz, that ores deposited from aqueous solutions are transported to their present positions by underground waters, that in order to transport this material an abundant circulation is required, and that in the deep-seated zone of anamorphism the circulation is a minimum, it follows that the waters derive their metals from the rocks of the zone of fracture. If any one asserts that the metalliferous materials of mineral veins are derived by water circulation from the centrosphere, or are derived from the lithosphere below the zone of rock fracture, I hold this to be a pure unverified assumption, for which there has not as yet been adduced one particle of evidence, and opposed to which stand well-known principles of physics concerning the movement of water in minute openings, and the condition of water in the deep-seated zone.

The conclusion that the waters derive their metals from the zone of fracture was reached as outlined on the foregoing pages, but since the publication of this conclusion the observational work of Lindgren upon metasomatic processes in fissure veins has fully confirmed it. Lingdren has made a careful study of the metasomatic changes in the wall rocks while ores and gangues are being deposited. He finds that the abundant minerals produced by metasomatic processes are quartz, fluorite, calcite, magnesite, dolomite, siderite, muscovite, chlorite, kaolinite, zeolites, and the sulphides.

He does not include epidote among the abundant metasomatic minerals of fissure veins, but it is certain that this mineral is important in certain deposits which are essentially the same as fissure veins so far as the circulating water is concerned. For instance, epidote is very important in connection with the Lake Superior copper. All of these minerals are shown (Chapters VI and VII) to be characteristic of alterations in the zone of katamorphism and especially of the belt of cementation. The carbonates are produced by the process of carbonation of the silicates, and the separation of quartz is the correlative process. The hydrous silicates are produced from the anhydrous silicates by a process of carbonation and hydration. For instance, Lindgren[a] says the muscovite is produced from orthoclase and microcline, and he thus writes the reaction:

$$3KAlSi_3O_8 + H_2O + CO_2 = KH_2Al_3(SiO_4)_3 + K_2CO_3 + 6SiO_2$$

It therefore appears that this reaction is one of hydration and carbonation, and at the time the muscovite is formed silica is liberated, to be deposited in the walls or in the veins.

According to Lindgren the kaolin is mainly formed by the alteration of feldspars, and especially the potassium and sodium feldspars. For potassium feldspar Lindgren writes the reaction:[b]

$$6KAlSi_3O_8 + 6H_2O + 3CO_2 = 3H_4Al_2Si_2O_9 + 3K_2CO_3 + 12SiO_2$$

Thus this reaction, like that of muscovite, is one of hydration and carbonation, but takes place to a greater extent, the resultant minerals being kaolin and quartz. It is not necessary to write here reactions for the zeolites, chlorites, and other hydrous minerals, for these may be found in Chapter V. An examination will show that the reactions producing them are those of hydration and carbonation of anhydrous silicates with the liberation of silica.

Lindgren mentions also, as subordinate minerals which form by metasomatic processes, rutile, anatase, garnet, orthoclase, albite, tourmaline, topaz, scapolite, and apatite. These minerals are those which commonly form in the zone of anamorphism. It has already been seen that in those cases in which it is shown that these minerals have developed at the same

[a] Lindgren, Waldemar, Metasomatic processes in fissure veins: Trans. Am. Inst. Min. Eng., vol. 30, 1901, p. 608.

[b] Lindgren, cit., p. 614.

time the ores were deposited as the dominant metasomatic minerals, the ores were probably formed in the zone of anamorphism or rock flowage, probably through the influence of gaseous solutions. The ore deposits which show these minerals as accompanying metasomatic products are few in number and unimportant in amount as compared with the ore deposits in which the metasomatic minerals are those of the first group mentioned. The point to be enforced at present is that the great mass of metasomatic minerals formed at the time the ore deposits are produced shows that these ores were deposited within the zone of fracture, or the zone of katamorphism.

This conclusion is confirmed by the close relations of the gangue minerals to the country rock. Where a vein runs through a quartzite or very siliceous rock, the gangue mineral is likely to be dominantly quartz. Where a vein runs through basic igneous rocks, the gangue minerals are likely to be largely zeolites and other hydrous silicates, carbonates, and quartz, all decomposition products of such rocks. Where the veins run through limestone the gangue material is likely to be mainly carbonate. It is therefore clear that the gangue minerals are largely segregated from the immediately adjacent rocks traversed by the veins. If this be so for the dominant minerals, there is every reason to believe that the same conclusion applies to the very subordinate amounts of valuable metals which constitute a small or almost an inappreciable part of the filling of an ore deposit. Numerous examples could be given illustrative of this principle. One of the best known to me is that of the Lake vein in the San Juan district. This vein, running through the volcanic breccias, extended into the limestone below, and from this into sandstone still lower down. Where the vein was in the breccia it was a quartzose vein carrying metals; when followed into the limestone it was seen to become a calcite vein, and when followed into the sandstone it gradually changed again into a quartz vein. In the limestone and sandstone the vein was barren. In this case it seems little short of certain that the vein filling was dominantly derived from the adjacent rock, and there is no reason to doubt that in the San Juan tuff the metalliferous material and the quartz alike were derived from the breccias.

While it is held that the waters derive the metals, as their immediate source, from the zone of fracture, it does not follow that the metal for the ores deposited from aqueous solutions may not have been derived from

greater depths; for, as fully explained (pp. 1030–1036), magma, carrying various metals with it, does rise from unknown depths into the zone of fracture upon an enormous scale, and there yields its metallic contents to circulating waters.

My third main conclusion is that the metals for ores deposited by aqueous solutions are derived from rocks within the zone of fracture.

III. WORK OF AQUEOUS SOLUTIONS IN SEGREGATING ORES.

The work of aqueous solutions in segregating ores is most complex. The ores produced by aqueous solutions may be divided into three subclasses—(1) ores precipitated from aqueous solutions by ascending waters, (2) ores precipitated from aqueous solutions by ascending and descending waters combined, and (3) ores produced by precipitation from descending waters. As the processes of segregation of each of these classes of ores are distinctive, each class will be considered in turn. In order to produce any of the ores of all these subclasses three stages of work need to be considered—the solution of the valuable metals, the transportation of them to the places where they are deposited, and their precipitation.

SUBCLASS 1. ORES PRECIPITATED FROM ASCENDING AQUEOUS SOLUTIONS.

There have been endless discussions as to whether ore deposits are produced by descending, lateral-secreting, or ascending waters. It is believed to be a corollary from what has gone before that the first concentration of many ore deposits is the result of descending, lateral-moving, and ascending waters. I say first concentration, for it will subsequently appear that many, if not the majority, of the workable ore deposits precipitated from aqueous solutions have undergone a second concentration. If the waters which deposit ores are mainly meteoric, such waters at the outset are descending. In most cases before they again issue at the surface they must ascend. During the journey they have a lateral movement.

Thus, the larger, more complete idea of the genesis of aqueous ore deposits comprises all of the old ideas, and shows that instead of being contradictory, as supposed by many, they are mutually supporting. Combined, they furnish a much more satisfactory theory than any one of them alone. How true these statements are will appear more clearly later.

While the subclass is named "Ores precipitated by ascending aqueous solutions," possibly a more exact heading would be either "Ores precipitated from solutions deficient in oxygen," or "Ores precipitated from deep solutions." From the chemical point of view the fundamental fact is that the solutions are deficient in oxygen. It follows from this that the solutions must be sufficiently deep or sufficiently protected from the surface to be free from oxidizing effects. Thus the subclass corresponds rather closely to Posepny's "Ores of the deep circulation."[a] But since the great majority of ores belonging to the subclass under discussion are deposited from solutions, the vertical element of which at the time of precipitation is ascending rather than descending, the heading chosen is given as the name of the subclass.

SOLUTION OF THE METALS.

In the first stage of the concentration of many deposits the waters are descending. They move slowly downward, are widely dispersed in small passages, have an exceedingly large surface of contact with rocks, and are subject to increasing temperature and increasing pressure. All of these conditions favor solution to the point of saturation. The various metalliferous elements present in exceedingly small quantities in the rocks, as well as many other compounds, are picked up. This follows from the law of physical chemistry, that a solution holds some part of all the elements with which it is in contact.

In the work of solution of the material for the ores, and in the deposition of it by the water, the two physical factors, temperature and pressure, are of great consequence. It is shown (Chapter III) that increase of temperature increases the activity of the water in two ways—first, the speed of the solution is very greatly increased by rise of temperature, and at temperatures of 100° C., and especially at a temperature of 185° C. and above, the activity of water is no less than amazing (p. 79). The effect of increase in temperature upon the activity of underground solutions can not be too strongly emphasized. It is also shown that as the temperature rises in general a larger quantity of material may be held in solution, at least for moderate increases of temperature, probably as high as 100° C. (pp. 79–81).

[a] Posepny, F., The genesis of ore deposits: Am. Inst. Min. Eng., 2d ed., 1902, pp. 1–72.

Under normal conditions of increase of temperature of one degree for 30 meters, the temperature would be 100° C. at a depth of 3,000 meters; therefore, where the circulation is deep, increase in temperature with depth, even under normal conditions, is of great consequence. But in many regions, during the segregation of ore deposits, igneous rocks have been intruded or extruded, or important orogenic movements have taken place, or both. Wherever igneous rocks have been intruded in the upper part of the lithosphere, or poured out upon the lithosphere during the time when ore deposits are forming, the temperature of the underground water is higher, and may be much higher than normal, so that even where ore deposits have been produced by a relatively shallow circulation the waters may have had the advantage of a high temperature. The temperature may increase with more than normal rapidity in consequence of mechanical and chemical action. Where there is no evidence of igneous intrusion during the time of ore deposition, but mechanical or chemical action has taken place upon a great scale, the temperature of the underground water may be raised considerably, and thus the deposition of the ores even in such cases be accomplished by solutions at higher temperatures than normal. For the underground solutions which occur in nature, pressure usually promotes solution. (See Chapter III.)

The particular metals and the amounts of them which are taken into solution also depend greatly upon the nature of solutions. To illustrate, where the solutions contain strong acids they are likely to dissolve the metals; where oxygen is abundant the sulphides are likely to be oxydized into sulphates and taken into solution; abundant carbonic acid forms carbonates; where alkaline sulphides and carbonates are present and the solutions come into contact with sulphides, these are somewhat readily dissolved as such.

While all of these compounds favor solutions, in the early part of the journey the most important single factor in the process of solution of the valuable metals is the presence of oxygen in the water. This is of great consequence, because many of the valuable metals, both as original compounds in the igneous rocks and as secondary products, are as sulphides. Where oxidizing waters come into contact with sulphides they are transformed to sulphates, and thus sulphates of most of the valuable metals may be formed, as, for instance, those of silver, copper, mercury, lead, zinc, iron,

arsenic, and antimony. All of these compounds are readily, or somewhat readily, soluble, with the exception of lead sulphate, which is soluble only to the extent of one part in 31,500 parts of water at 15° C.[a] But even this degree of solubility is entirely adequate to account for the transportation of the lead as a sulphate.

While the effect of the oxygen is to transform the sulphides to sulphates, it is not supposed that the metals necessarily travel as such salts. The well-known principles of physical chemistry make it certain that each of the metals present in solution is combined in part with each of the acids. For instance, if silver sulphide be oxidized to sulphate, and sodium carbonate be present in the underground solutions, as is sure to be the case, then a part of the silver will be transformed to silver carbonate and the sodium will travel in part as sodium sulphate. In this connection the point is that the sulphides get transformed through the agency of oxygen to compounds which are much more readily soluble.

It is further to be remembered that in the upper part of the course of descending water, where oxygen is abundant, *ic* salts are produced. Of these the sulphates are most abundant, but with them are chlorides also. Of these *ic* salts, ferric sulphate and chloride are very prevalent.

In salts of this class metallic gold and silver are dissolved. The solution is controlled by the law of mass action and by the temperature. The greater the amount of the salts present, and the higher the temperature, with a given amount of salts, the more gold and silver may be dissolved. Thus, descending solutions are those in which *ic* salts are abundantly formed and in which the temperature is increasing. Both the abundance and the increasing temperature are favorable to the solution of gold and silver.

Therefore we conclude that *the solutions which perform the first work in the genesis of ore deposits, the dissolving of the metals, are descending.*

TRANSPORTATION OF THE METALS.

Superimposed upon the downward movement of the waters is a lateral one which, combined with the vertical movement, carries water sooner or later to the trunk channels. The amount of water taking part in the lateral movement is greatest near the surface of ground water, and from that

[a] Comey, A. M., Dictionary of chemical solubilities: London, 1896.

surface on the average decreases to the bottom of the zone of fracture. It has been explained that all fissures and other openings gradually die out below as the zone of rock flowage is neared. (See pp. 187–191, 766–768.) Therefore, for a given fissure, the waters enter it mainly from the side or top, not from the bottom. Furthermore, the water does not enter the fissure at a single place, but at numberless points all the way along its course, from the deepest parts to the surface. Somewhere, however, the water which enters a fissure must flow from it. This place may be at the

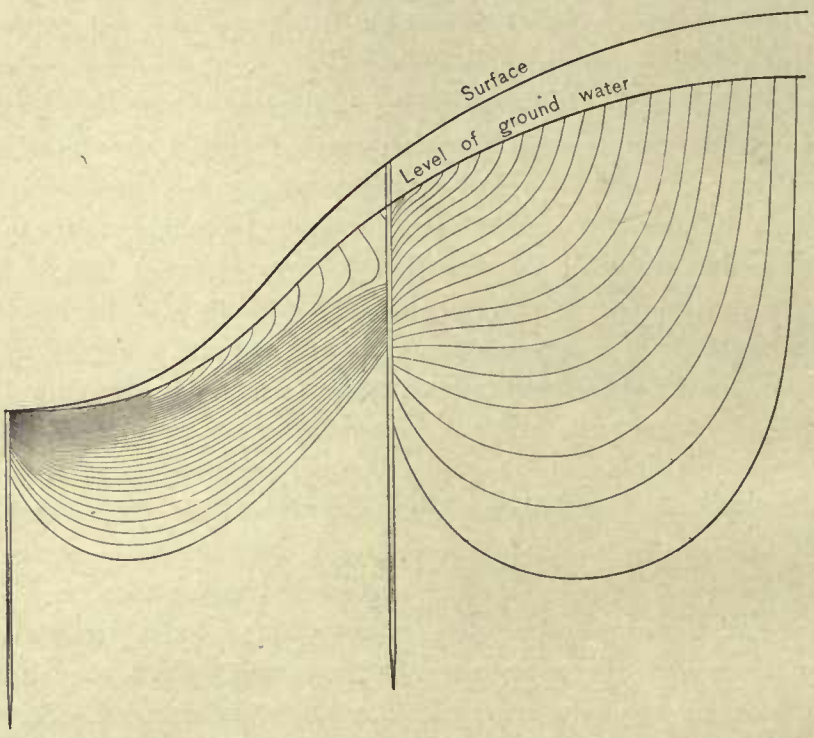

FIG. 26.—Ideal vertical section of the flow of water entering at a number of points on a slope and passing to a valley below through a homogeneous medium interrupted by two open vertical channels, one on the slope and one in the valley.

surface or at a considerable depth below the level of ground water. (See fig. 26.) The streams entering the fissure at high levels may have a downward movement and contribute water abundantly. Below the level at which water escapes laterally from a channel of given size the water contributed to it decreases on the average with increase of depth, until in the deeper part of the zone of fracture the contributions are very small. Posepny[a]

[a] Posepny, F., Genesis of ore deposits: Trans. Am. Inst. Min. Eng., vol. 24, 1875, p. 971. Also Posepny, F., The genesis of ore deposits, Am. Inst. Min. Eng., 2d ed., 1902, pp. 242–243.

calls attention to the frequently observed fact of the decreasing amount of water contributed laterally as depth increases. As a specific instance of this, he mentioned the Przibram district, in which the amount of water entering the fissures below a depth of 300 meters is so small as to be insignificant, but this may not have been the fact at the time the lode was forming. (See pp. 1063–1065.)

While the amount of water laterally entering a fissure decreases from near its top to the bottom, the amount of mineral material per unit volume in all probability increases on the average; for the waters entering at a low level take a longer journey through smaller openings and at higher temperatures and pressures than the waters entering at a high level. Therefore it is clear, if the rocks with which the deeper water comes in contact can furnish metalliferous materials, that such water will be heavily loaded. It follows from this, even if the amount of water which is furnished in a short time to a fissure be small, that such water may furnish from the country rock mineral material in solution much more than sufficient to entirely fill a fissure during its long life.

We now understand that, on the average, the amount of water entering a fissure decreases from the level of ground water to its bottom, but that the amount of mineral matter brought into the fissure by the water (but not necessarily deposited) increases per unit volume from top to bottom. It is, therefore, impossible to make a general statement as to whether more mineral material is contributed to a trunk channel in its upper portion or in its lower portion. Doubtless this varies in different cases. Other conditions than amount of water or depth may be controlling factors. For instance, if igneous rocks be intruded at high or low levels only, such rocks may furnish conditions which determine the amount of metalliferous material contributed by the waters.

While the foregoing paragraphs imply that the lateral moving waters are also downward moving, this is meant only as a general rule. The lateral movement may be accompanied by no downward movement. Not only this, but lateral movement may be accompanied by an upward component. Indeed, this is believed to be very frequently the case, especially so far as the main branch streams in the deeper parts of the zone of fracture are concerned. In so far as there is an upward component in these branch streams, the reactions which obtain are the same as those of the trunk channels to be considered below.

During the lateral journey of the water, before trunk channels are reached, the transported metals may be largely precipitated. Frequently such precipitates are very widely dispersed and are not sufficiently rich to constitute ore deposits. Exceptionally the amounts of precipitated material during the lateral movements in the dispersed channels may result in the formation of a product of sufficient richness to constitute an ore. Precipitation may result from any of the causes or combinations of causes which are spoken of (pp. 1081–1088; see also pp. 113–123) as producing precipitation from ascending waters in trunk channels. For the purpose of illustration, one class of compounds may here be mentioned. Salts traveling as sulphates may be reduced to sulphides and precipitated by the direct reactions of carbonaceous materials, by the reaction of previously precipitated sulphides, or, in the case of copper, silver, etc, by the reaction of abundant ferrous compounds. The Crystal Falls volcanics[a] furnish an illustrative case where rocks have been so profoundly altered by metasomatic changes as to leave scarcely an original mineral present. In them there are sparse, widely disseminated secondary sulphides. In this formation there is no organic material, and the natural cause to assign for the precipitation is the reducing action of the ferrous compounds which are abundantly present. The possible reactions are given on pages 1111–1112.

From the foregoing *it appears that ores are carried to trunk channels by laterally moving waters. Lateral secretion is, therefore, an essential step in the first concentration of ore deposits*, although I use the term lateral secretion in a broader sense than did Sandberger.

The places where the ore deposits themselves are found will now be considered. As already noted, these occur mainly in or adjacent to the more continuous larger openings. These openings are occupied by the trunk streams of circulating waters, and therefore the water is in the latter part of its course. Hence these trunk streams, as has already been shown (p. 583), have in general an upward rather than a downward vertical movement. The waters reaching the trunk channel at any point immediately begin their ascent. At any given cross section of a channel there must pass all of the water contributed below. At great depth this amount has already been seen to be small. From a small amount the waters steadily increase in

[a] Clements, J. Morgan, and Smyth, H. L., with W. S. Bayley, The Crystal Falls iron-bearing district of Michigan: Mon. U. S. Geol. Survey, vol. 36, 1899, pp. 73–154.

volume to the point where they begin to escape laterally. (See fig. 26.) Hence in a trunk channel of a definite size the circulation is slow below and increases in speed above. Near the bases of the channels from which the Mammoth Hot Springs and geysers of the Yellowstone Park issue the amount of water contributed may be small and the movement of the water may be exceedingly slow. Even if true, as held by some, that rapid movement of water is unfavorable to deposition of ores, it is wholly possible that at moderate depth, especially in the deeper parts of a channel from which the flow at the surface is rapid, the conditions are those of slow movement and rapid precipitation of ore deposits.

As the water passes upward the variety of solutions as well as the amount increases, for each stream differs in its salts from every other, since no two streams can possibly have had exactly similar histories. Moreover, the character of the wall rock may vary from place to place. The pressure and the temperature also lessen. These conditions are favorable to precipitation. *Therefore many ores in their first concentration are precipitated by ascending waters.*

It is now clear that a satisfactory account of the genesis of ores includes ascending waters. Many ores in their first concentration are actually precipitated from the ascending waters, and therefore emphasis has been placed upon this part of the work of circulating waters.

The broader statement of the genesis of a great class of ore deposits is that the water after penetrating the earth is widely scattered in contact with rocks in innumerable minor openings. These waters travel downward with steadily increasing pressure and temperature. They take up the constituents of the ore deposits. The downward movement of the waters has superimposed upon it a lateral component, as a result of which the waters are carried to the larger openings. During this process also the waters continue to take material into solution. In the larger openings where the waters are congregated they are upon the average ascending with decreasing temperature and pressure, and the ores are precipitated.

While it is believed that in the great majority of instances the journey of the underground water involves first a descending and later an ascending movement, it is recognized that this is not invariably the case. Upon the descending movement may be superimposed a lateral movement which brings the water to the surface again at a lower level, there being at no

time an important ascending movement. This is especially likely to occur in districts of great topographic relief, where the descending waters strike an inclined impervious plane dipping toward a valley. (See fig. 27.) In the case illustrated the water falling on the mountains percolates downward through the rocks until it comes into contact with an impervious stratum, which it follows toward the valley until it issues above the stream, having nowhere during its journey an ascending component.

While it is held, as explained above, that upon the whole the descending waters are dissolving material and the ascending waters are depositing

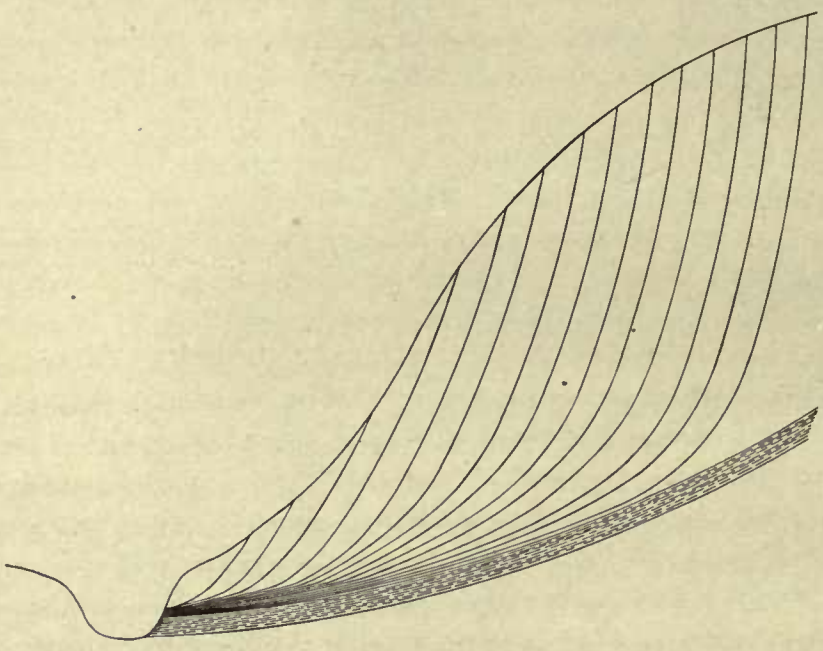

FIG. 27.—Ideal section showing underground circulation in which no water anywhere ascends before issuing at the surface.

material, it is not meant to imply that materials are not deposited by descending and lateral-moving waters, nor that materials are not dissolved by ascending waters. Indeed, it is certain that solution and precipitation are taking place at all times throughout the entire course of all the branches of the underground circulation. This is a necessary consequence of the laws of physical chemistry. It is meant only to imply that in the first concentration of one class of ore deposits, solution so far as the ores are concerned is the rule for the descent and deposition for the ascent, although there is no doubt that there are many local exceptions to this.

It is, of course, understood that the underground circulation in any actual instance is much more complex than that given in the simple ideal case which has been considered. For instance, it is certain that, in the same mineral-bearing area, immediately adjacent trunk channels may have had very different histories. This is especially well shown by the deposits at Butte, Mont., where there are two parallel main zones of mineralization, only a short distance apart, the mineral wealth of one of which is mainly copper, while that of the other is mainly silver.[a] Many of the other special factors which modify the simple general statement above given are discussed on pages 1199–1222.

PRECIPITATION OF THE METALS.

The precipitation of metals in the trunk channels by ascending waters is of so much importance in the concentration of ores that this process needs further consideration.

Precipitation may take place (1) by change in temperature and pressure, (2) by mingling of solutions, and (3) by reactions between solutions and solids. (See pp. 113–123.)

PRECIPITATION BY DECREASE OF TEMPERATURE AND PRESSURE.

The general relations of solution and precipitation as a consequence of varying temperature and pressure have been already considered. (See pp. 114–116.) Where the increase of temperature with depth is normal, it has been seen that decreasing temperature and pressure due to the ascension of waters from a depth of at least 3,000 meters are favorable to precipitation. Furthermore, the same statement holds even if the increment of temperature be greater than normal, provided the temperature does not greatly exceed 100° C. Cases in which water issues at the surface at such temperatures are very rare. The probably decreasing pressure and temperature of solutions rising from depths greater than 3,000 meters are also favorable to precipitation. Since it has just been shown that ascending waters are likely to be in trunk channels, lessening temperature and pressure are likely to produce precipitates in the openings of faults, joints, and bedding partings, and the more open places in sandstones, conglomerates, and amygdaloids.

Since upon the average ascending solutions are those in which the pressure and temperature are decreasing, precipitation is more likely to

[a] Emmons, S. F., Notes on the geology of Butte, Mont.: Trans. Am. Inst. Min. Eng., vol. 16, 1888, p. 54.

occur from them in consequence of change of temperature and pressure than from descending solutions.

When one attempts to apply these general statements to specific metals, experimental data are lacking. It is undoubtedly true that decreasing temperature and pressure are much more influential in the precipitation of some metals than of others. Until experimental work has determined how the various economic metals respond to changing temperature and pressure, it is impracticable to specify the ores in which precipitation is more strongly favored by decrease of temperature and pressure. One would expect that precipitation as a consequence of changing temperature and pressure would tend to give a somewhat orderly vertical distribution of the various metalliferous ores.

As an illustration of the influence of a decrease of temperature we may take the cases of gold and silver. It is well known that gold is precipitated by cuprous chloride, according to the following reaction:

$$AuCl_3+3CuCl=Au+3CuCl_2$$

Silver is precipitated by ferrous sulphate according to the following reaction:

$$Ag_2SO_4+2FeSO_4=2Ag+Fe_2(SO_4)_3$$

Under given conditions, if a sufficient amount of time be allowed, these reactions will proceed until equilibrium is reached. Stokes has shown that if the temperature is decreased, after equilibrium is reached, these reactions will proceed further, but if the temperature is increased the reactions reverse and the gold and silver are dissolved. Therefore, where for a given temperature these solutions are saturated with silver and gold, and the temperature is decreased, precipitation of the metals will result.

PRECIPITATION BY MINGLING OF SOLUTIONS.

Precipitation in the trunk channels is produced by reactions caused by the mingling of various solutions. The mingled solutions may be gaseous and aqueous, or all aqueous. Precipitation by reactions between aqueous solutions and gases is especially likely to take place near the level of ground water, where gases from the belt of weathering mingle with the solutions of the belt of cementation.

Precipitation by reactions between aqueous solutions is especially likely to take place at the intersections of trunk channels, where aqueous solutions

from different sources meet. Such precipitation takes place under the general law that when solutions of two or more kinds are mingled, if a substance can form which is insoluble in the liquids present, this compound will be produced and precipitation take place. This mingling of solutions is probably the most important of the causes of precipitation of ores.

It is evident that solutions from different sources enter a given trunk channel at many places and thus a multitude of streams with different composition mingle in a trunk channel. Each of the incoming streams is different from any of the others, although in many cases the difference may be slight. As a case of certain considerable difference may be mentioned ascending and descending streams. (See pp. 1175–1177.) If in a chemical laboratory a multitude of solutions be taken at random and thrown together precipitates will be almost certain to form, and in an underground channel the same effect is likely to be produced when the various solutions come together. This mingling of solutions is one of the most important of all the factors which results in the deposition of the ores. I have little question that the wide variety of solutions which enter a given channel explain in a large measure the exceedingly irregular richness of ore deposits. Where a metal is found abundantly in a fissure the explanation in many cases is certainly that at or near that place there entered a stream which carried either the precipitated metal or an agent capable of precipitating it from a solution already in the trunk channel. For instance, it is believed that at or near the place where the great bonanza of the Comstock lode was found, there entered either solutions rich in gold and silver, or a solution having a compound which precipitated the gold and silver already traveling upward within the lode. Perhaps the former hypothesis is the more probable.

Ore shoots, or chimneys of ore of exceptional richness, occur very frequently in veins. They are sometimes parallel with the dip and at other times pitch to the right or left of it. The locations of these ore shoots in many instances I believe were controlled by cross fractures or joints through which entered waters, carrying either metalliferous material or solutions capable of precipitating the metalliferous mineral in the trunk channel at the place where the lateral streams of water entered.

The lead and zinc deposits of the Mississippi Valley, according to Jenney, are larger at the crossings of two sets of fissures than elsewhere. This may be explained partly by the greater abundance of the solutions

furnished by two sets of fissures, but, as suggested by Jenney,[a] partly by the mingling of two different kinds of waters, thus giving conditions favorable for precipitation.

In the Enterprise mine, at Rico, Colo., described by Rickard,[b] the ore bodies are in vertical veins and in flats under shales. While a set of cross veins is barren, "the rich ore bodies overlie them in the contact zone."[c] Below the shale it is common to find ores of more than average grade in the pay veins where they are broken by the cross veins. It is believed the explanation of these relations is the reactions resulting from the mingling of the solutions of the "verticals" with the inclined cross veins. With this Ransome's recent studies accord. He says: "Large bodies of workable sulphide ore occur only where the solutions in the lode fissures have had opportunity to mingle with laterally moving solutions in the blanket."[d]

The silver-lead deposits of the Aspen district of Colorado, described by Spurr, furnish an instance of very probable precipitation of rich ore shoots by the mingling of solutions. Spurr states that generally an ore body is "found at the intersection of two faults, one of these faults usually dipping steeply, while the other is much flatter." For this "the explanation is offered that by the mingling of solutions which had previously flowed along different channels the precipitation of metallic sulphides was brought about."[e]

Probably the rich shoots of gold ore in the Sierra Nevada, which, according to Lindgren, pitch to the left as one looks down the vein, further illustrate the principle of precipitation by mingled solutions. For the most part, Lindgren makes no statement as to the relations of ore shoots and lateral seams. However, on Canada Hill vein there are "occasional rich bunches at the intersections" of the two systems of veins.[f]

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[a] Jenney, W. P., The lead and zinc deposits of the Mississippi Valley: Trans. Am. Inst. Min. Eng., vol. 22, 1894, pp. 189–190, 224.

[b] Rickard, T. A., The Enterprise mine, Rico, Colo.: Trans. Am. Inst. Min. Eng., vol. 26, 1897, pp. 906–980.

[c] Rickard, cit., p. 977.

[d] Ransome, F. L., The ore deposits of the Rico Mountains, Colorado: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, p. 301.

[e] Spurr, J. E., Geology of the Aspen mining district, Colorado: Mon. U. S. Geol. Survey, vol. 31, 1898, p. 234.

[f] Lindgren, Waldemar, The gold-quartz veins of Nevada City and Grass Valley, California: Seventeenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1896, p. 195.

It is believed that the Cripple Creek deposits likewise illustrate this principle. Penrose[a] notes that many of the rich ore shoots occur at cross fissures. It is thought probable that the main cause for the formation of ore shoots at such places is the reaction of solutions furnished by one set of fissures upon those furnished by the other set. It is but fair to say, however, that Penrose makes the explanation, the "mechanical one, in deflecting the course of the ore-bearing solutions."

What are the reactions which result in precipitation from the mingling of solutions? It has been pointed out (p. 1075) that in the upper part of the journey of descending waters *ic* salts are likely to be present. In the deeper parts of the belt of cementation, where organic matter and ferrous compounds are abundant, these *ic* salts are commonly changed to *ous* salts, and such salts are abundant. Such solutions are likely to make their way into the trunk channels. If they there meet salts of gold, silver, or copper, these compounds may be thrown down. This is likely to take place if the reducing solutions are abundant. That is, the reaction is under the law of mass action. It has already been seen that this reaction is promoted by decreasing temperature. Another reaction frequently resulting in the precipitation of sulphides follows from the mingling of solutions, one of which bears hydrogen sulphide and the other sulphates or other oxidized salts. In trunk channels the mingling of solutions of these kinds must be very common, the oxidized solutions coming perhaps somewhat directly from the surface, whereas the hydrogen-sulphide solutions have usually taken a longer journey in the belt of cementation, and thus have taken on a reducing character.

While the above explanation may in many cases account for apparent irregularities in the kinds and percentages of metals, other principles are needed to explain the fact that metals occur in a definite order from the surface downward and that many valuable metalliferous ores grow poorer at a depth of 1,000 meters or less. Varying temperature and pressure are important in this connection; but more influential in many instances, as will be shown subsequently, is a second concentration produced by descending waters.

[a] Penrose, R. A. F., jr., Mining geology of Cripple Creek, Colorado: Sixteenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1895, pp. 164–165.

PRECIPITATION BY REACTIONS BETWEEN SOLUTIONS AND SOLIDS.

Precipitating reactions between the solutions and solids with which they are in contact often take place. The solid wall rock frequently produces precipitations of metalliferous ores from the solutions in the trunk channels in the following ways: (1) It has already been explained that a solid, when placed in contact with a liquid, may precipitate some compound previously held in solution, some part of the solid going into solution at the same time. Thus, the wall rock may precipitate ores. (2) The wall rock furnishes the trunk solutions with precipitating solutions, which may precipitate metals already in solution within the trunk channels. (3) The wall rock itself may supply the ore deposit with metalliferous material, which, when it reaches the trunk channel, may be precipitated by the solutions there contained. Where the wall rock is easily soluble, enlargements of the openings occur readily and afford places for the deposition of the metalliferous material. (See pp. 1212–1216.)

The reactions due to the country rock are likely to be effective in proportion as it is porous and soluble and therefore allows solutions to permeate and to dissolve it. Thus the country rock is likely to be especially effective in its reactions where the trunk channel is a complex one and gives a large surface of action. It is believed that the effect of the wall rock in these various ways is of great importance in the production of many ore deposits.

As an illustration, may be cited the very general association of lead, zinc, and copper ores, and the accompanying gold and silver, with limestone. It is well known that in many cases ore deposits in limestone are large and rich, and in the associated rocks are small and barren. This is illustrated by the lead and zinc deposits of the Mississippi Valley, which occur almost exclusively in limestones, although these rocks are interstratified with sandstones. Where the openings pass into sandstones the ore deposits become small and poor or die out altogether. Precisely the same relation is illustrated in the copper deposits of the Southwest. Here the ores are very largely in the limestone, and when they pass into the acid associated rocks, either sediments or porphyries, become small, and often fail.[a]

[a] Douglas, James, The Copper Queen mine, Arizona: Trans. Am. Inst. Min. Eng., vol. 29, 1900, pp. 512–513. Ransome, F. L., The copper deposits of Bisbee, Arizona: Eng. and Min. Jour., vol. 75, 1903, pp. 444–445.

Many other similar illustrations could be given. It is recognized that these relations are explained in part by the ready solubility of the limestones as compared with the acid rocks, thus giving openings for the deposition of ores, but also largely, it is believed, by the reaction of limestone, or its solutions, upon the solutions which contributed the metals. This conclusion, already announced from the geological relations, without reference to experimental work, has been confirmed by laboratory work by Mr. H. N. Stokes. Mr. Stokes has shown that when soluble zinc, lead, copper, or silver salts are heated with iron bisulphide, in the presence of an alkaline carbonate, the metals are thrown down as sulphides. The reactions are given on p. 1117. It was suggested that calcium carbonate might be substituted for the sodium carbonate and similar reactions take place, and this Mr. Stokes found to be the fact. It is therefore certain that where limestone is the wall rock it often has a very important influence in the precipitation of the ores.

The supposition that the limestones are a cause of precipitation does not preclude the possibility that they may not also contribute the metals, as in the case of the lead of the Mississippi Valley. But in such cases the precipitation is probably due more to the mingling of solutions in trunk channels than to the effect of the wall rock. Of course, in some cases, the association of ore with limestone may be due to more than one of the factors mentioned—the ready solubility of the limestone, its power to cause direct precipitation, to furnish precipitating solutions, and to supply the metals or some part of them.

Another case of precipitation resulting from the influence of the wall rock is the well-known occurrence of metallic copper in the openings of sandstones, conglomerates, and amygdaloids of Keweenaw Point.[a] The metallic copper between the particles was doubtless precipitated by ferrous solutions furnished by the wall rocks, which in many cases are basic volcanics.

A particularly clear illustration of the effect of wall rock is furnished by ores in which the sulphides are confined to strata containing organic matter, as in some copper deposits[b] and some of the gold reefs of Australia.

[a] Irving, R. D., The copper-bearing rocks of Lake Superior: Mon. U. S. Geol. Surv., vol. 5, 1883, pp. 419–430.

[b] Posepny, F., The genesis of ore deposits, and Cazin, F. M. F., discussion of same: Trans. Am. Inst. Min. Eng., vol. 23, 1894, pp. 316, 606–607.

In the case of the copper deposits the organic matter has in all probability reduced sulphites or sulphates to sulphides. The function of the organic matter in the case of the gold may have been to reduce it to metallic gold, or to produce *ous* salts, for instance, ferrous sulphate, which reduced the gold. (See pp. 1093–1095.)

GENERAL STATEMENTS.

In conclusion, it may be said that the precipitation of metallic ores by the mingling of various solutions is probably the most important single factor which results in the first concentration of ores. Probably next in importance to this are the reactions upon the trunk streams, due to the wall rocks. As lateral streams from beyond the wall rocks must pass through the latter, many of these streams produce an effect due partly to materials more remote than the wall rocks and partly to the wall rocks. Thus in many cases the effect of solutions originating beyond the wall rocks and that of solutions furnished by the wall rocks may not be discriminated. Diminishing temperature and pressure, while probably subordinate in their effect to the mingling of streams and reactions due to the wall rocks, are in many instances undoubtedly important, and in some instances dominant, factors. In general, the tendency of writers has been to emphasize the effect of diminishing temperature and pressure, and to minimize or even disregard altogether the effects of mingling solutions or the wall rocks, or both.

Precipitation in many cases is not produced by a single one of the factors, but by two or three of them. For instance, precipitation may be produced by the joint effect of a change in pressure and temperature, by the reaction between gases, solutions, and solids, and by the combination of change in pressure, change in temperature, and the mingling of solutions. In short, all possible combinations of the various causes of precipitation may and do occur in connection with ore deposits.

COMPOUNDS DEPOSITED BY ASCENDING SOLUTIONS.

Of the metallic ores those of iron, copper, lead, zinc, nickel, silver, gold, and mercury are the more important. These metals vary greatly in the forms in which they are precipitated. The deposits formed by ascending water occur in the metallic form, as sulphides, tellurides, oxides, carbonates, and silicates. The metals deposited in the metallic form in impor-

tant amounts by ascending water at the first concentration are silver, gold, and copper. Metallic gold, copper, and silver are also produced in connection with the reactions of descending water, but such deposits are not here considered. Their development is treated on pages 1158–1174. All of the metals mentioned, with the exception of gold, occur in the form of sulphides. The sulphides are either simple binary salts or are ternary salts, such as sulpharsenites, sulpharsenates, sulphantimonites, and sulphantimonates. The sulpharsenical and sulphantimonical compounds will not be considered separately from the simple sulphides. The important tellurides are those of silver and gold. An important oxide deposited by ascending water is magnetite, and possibly franklinite and zincite belong here. Of the carbonates that of iron is of the greatest consequence. Of the silicates that of zinc may belong here. Of course many other oxides, carbonates, and silicates are found in ore bodies; but so far as these are in sufficient abundance to constitute workable ore deposits, it is believed, as will be fully explained later, that these compounds do not belong to the class of ores deposited by ascending water.

Why compounds deposited by ascending waters are, for the most part, not oxidized compounds, but metallic compounds, sulphides or tellurides, is easily explained. The widely disseminated, downward-moving water, bearing oxygen, is robbed of this constituent early in its course. Ferrous compounds are abundantly present in the rocks in the forms of magnetite and silicates. Iron is a strong base; and where ferrous compounds are present they continue to abstract the oxygen of the downward-moving waters until it has practically disappeared. Moreover, buried organic matter takes oxygen from underground waters. Hence oxidizing compounds do not exist in the deep-seated ascending water.

METALS.

GOLD.

Solution.—It has been stated that gold is deposited by ascending waters in important amounts. The manner in which gold is dissolved and transported to the greatest extent in underground solutions is not well known. As a matter of experiment it has been long known that gold is soluble in ferric chloride and in cupric chloride. Doelter has shown that gold is somewhat readily soluble in a 10 per cent solution of sodic carbonate, and also

in an 8 per cent solution of sodic carbonate containing an excess of carbonic acid and containing sodic silicate.[a] Becker has shown that gold is easily soluble in sodic sulphide and in sodic sulphydrate.[b] It has also been held that gold is soluble in ferric sulphate. Recently Stokes has experimentally investigated the solubility of gold. He finds that gold is somewhat readily soluble at a temperature of 200° C. in solutions of ferric chloride and cupric chloride according to the following reactions:

$$Au+3FeCl_3 \rightleftarrows AuCl_3+3FeCl_2$$
$$Au+3CuCl_2 \rightleftarrows AuCl_3+3CuCl$$

It thus appears that when gold is dissolved by ferric chloride or cupric chloride it is transformed to a chloride. The greater the amount of these chlorides and the stronger the solutions the more gold may be dissolved. With a given amount of ferric chloride or cupric chloride, with constant temperature, the reactions cease when equilibrium has been reached. Stokes's work has further shown that when this condition exists a rise in temperature causes the reaction to continue. That is to say, with increasing temperature a given amount of ferric or cupric chloride in a given solution is capable of taking an increasing amount of gold into solution.

Stokes finds that gold is not appreciably dissolved in ferric sulphate unless chlorides are present at the same time, thus furnishing ferric chloride and making the solution really that by the reaction already given. His experiments have not been carried to sufficient refinement to prove that ferric sulphate may not dissolve gold to an extent to be of consequence in the segregation of the metals under natural conditions.

Lenher, in advance of publication, has kindly given me the results of experiments which show that gold is soluble in sulphuric acid, phosphoric acid, and various other acids, if a compound be present which liberates oxygen, as, for instance, manganese dioxide. The reaction takes place at 0° C., but is greatly accelerated by heat. This principle may be of considerable importance in the solution of gold, since all of those compounds occur rather plentifully under natural conditions. The frequent association of gold ores with manganese minerals strengthens this suggestion.

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[a] Doelter, C., Einige Versuche über die Löslichkeit der Mineralien: Tschermaks Mineral. Mittheil., vol., 11, 1890, p. 329.

[b] Becker, G. F., Geology of the quicksilver deposits of the Pacific slope: Mon. U. S. Geol. Survey, vol. 13, 1888, p. 433.

The conclusion that gold is soluble in ferric and cupric chlorides, in acids where oxygen is liberated, and is possibly soluble in ferric sulphate, and that these processes are promoted by increasing temperature, is of the greatest importance in reference to the segregation of gold. It has been pointed out that the *ic* salts are those which are extensively produced in the belt of weathering by descending solutions. Iron sulphide is the most abundant sulphide. By the reaction of oxygen upon it ferric sulphate is produced, and by its decomposition sulphuric acid. Ferric chloride would form wherever chlorine is present. If copper sulphides occur, these would be transformed to similar salts. Thus in the belt of weathering considerable quantities of the solvents of gold are formed. In connection with the production of a large amount of these reagents where the solutions are descending, the law of mass action leads to the conclusion that the gold will be dissolved somewhat in proportion to the mass of these compounds produced. Furthermore, where the solutions are descending there is a rise in their temperature, and the work of Stokes shows that this further increases their activity. Hence, under normal conditions in a region of mineralization where there are sulphides and where gold exists, one would expect that the dispersed descending solutions would dissolve gold in considerable quantity.

Precipitation.—In whatever form gold is carried it is known to be precipitated in the first concentration as metallic gold or as a telluride. Whether it is also precipitated as a sulphide is uncertain.

It is easy to suggest various causes for the precipitation of metallic gold from its solutions. First, it is well known that gold solutions are immediately precipitated by the more basic metals. Of these metals there is likely to occur underground those of copper, silver, and tellurium. Occasionally also iron may occur. The rapid precipitation of gold from its solutions by contact with iron, copper, and silver are well known.

Recently Hall and Lenher have shown that tellurium completely precipitates gold from its solutions according to the following reactions:[a]

$$4AuCl_3+3Te=4Au+3TeCl_4$$

They state: "Time is a considerable factor in bringing about complete precipitation, from two to three hours being necessary with continued

[a] Hall, R. D., and Lenher, Victor, Action of tellurium and selenium on gold and silver salts: Jour. Am. Chem. Soc., vol. 24, 1902, p. 919.

heating, or several days at room temperatures. The only conditions to be observed, in order to obtain quantitative precipitation of the gold by the tellurium, are sufficient time and the direct contact of all the tellurium with the gold solution."[a] Hall and Lenher have also shown that selenium precipitates gold from its solutions in a similar manner according to the reaction:

$$4AuCl_3+3Se=4Au+3SeCl_4$$

They say: "From six to eight hours of continued boiling are necessary to insure complete precipitation, or better, from two to three days at a temperature of 70° to 80°."[b]

Not only is gold precipitated from its solutions by various metals, but it is precipitated by many *ous* salts and oxides; for instance, it is well known that ferrous sulphate readily reduces gold to the metallic condition. Stokes has recently shown also that ferrous salts in silicates are sufficient to precipitate copper from its solutions, and if this be so, it is certain that gold may be precipitated in like manner. There is little doubt, also, that ferrous oxide in magnetite is adequate to precipitate gold from its solutions. It is to be noted that Stokes writes the equations

$$AuCl_3+3FeCl_2 \rightleftarrows Au+3FeCl_3$$
$$AuCl_3+3CuCl \rightleftarrows Au+3CuCl_2$$

as reversible reactions. He states that "with rising temperature the equilibrium moves from left to right, with falling temperature from right to left."[c]

It follows that where there is lessening temperature and pressure, ferrous chloride and cuprous chloride reduce gold solutions, throwing down the metallic gold. Normally, the conditions for falling temperature are those for ascending solutions, and therefore, so far as gold is precipitated by these reactions, it is more likely to take place where the waters are ascending.

So far as I know, experiments have not been made in the precipitation of gold by cuprous oxide and cuprous salts other than cuprous chloride; but in general it may be stated with a considerable degree of certainty that any of the ferrous and cuprous compounds which occur in nature are adequate precipitating agents for gold solutions. From the descriptions of

[a] Hall and Lenher, cit., p. 920. [b] Hall and Lenher, cit., p. 921. [c] Stokes, manuscript, p. 7.

various gold deposits it seems to me very probable that in many instances the ferrous salts have been important reducing agents, and the same may be true of cuprous compounds.

It has been seen on a previous page that the *ic* compounds capable of dissolving gold are produced extensively in the early part of the journey of underground water. It has further been fully explained (p. 1085), that deep in the belt of cementation, where organic matter and sulphides are abundant, *ic* salts are changed to *ous* salts, which are the prevalent compounds deep within the belt. Therefore the trunk channels which carry the gold in solution are likely to receive contributions from other solutions which carry *ous* salts in large amount. Here the conditions are just the reverse of those existing in the early part of the water's journey. The law of mass action now demands the reduction of the gold to its metallic condition. For instance, if the gold were a chloride, and ferrous sulphate were present, the following reaction would take place:

$$2AuCl_3+6FeSO_4=2Au+2Fe_2(SO_4)_3+2FeCl_3$$

Similar reactions are written for ferrous chloride and cuprous chloride on the preceding page. It is also to be remembered that in trunk channels the solutions are likely to be ascending. Therefore the temperature is falling, and as pointed out by Stokes all of these reactions are promoted by this condition. Thus an abundance of reducing solutions and the temperature both work together to produce precipitation in the trunk channels.

In connection with these reactions the question naturally arises as to which of the *ous* salts is probably the most important. Since iron is the most abundant of all the metals carried in underground solutions, such sulphates would be more likely to be sulphates of iron than any other. If the salts formed in the belt of weathering were ferric sulphates, they would be likely to be reduced to the ferrous condition at depth by organic matter or by sulphides. Indeed, analyses of mineral waters which bear sulphates also ordinarily show ferrous iron.[a] Therefore ascending waters bearing ferrous sulphate or other *ous* salt might be brought into a lode by side streams and there precipitate the gold. Such side channels entering through lateral cracks may, in many cases, cause the extreme irregularity in the distribution of the gold.

[a] Peale, A. C., Mineral waters of the United States: Bull. U. S. Geol. Survey No. 32, 1886.

Although Lindgren argues to the contrary with regard to the Sierra Nevada,[a] the suggestion that a part of the gold there has been reduced by ferrous sulphate has extreme plausibility. The gold associated with the pyrite is native. From that district are given two analyses of the waters of feeding streams (the only analyses reported) entering the lodes at a depth of 125 meters. Both of these analyses show that sulphates and iron are present.[b] According to the analyses the iron is reported as ferric; but apparently no precautions were taken, when the waters were collected, to prevent the oxidation of ferrous to ferric iron. Indeed, the precipitates of yellow material, which is partly ferric oxide, made by underground springs renders it highly probable that ferrous salts were contained in them before oxygen came into contact with the solutions. The clean vein quartz itself, which holds a large number of fluid inclusions, contains sulphates,[c] showing that sulphate-bearing waters were present at the time the lodes formed.

The ore shoots have great irregularities in richness, for which Lindgren offers no explanation. The suggestion above made that the gold is precipitated in the metallic form by the reducing action of ferrous sulphate explains all of these facts. The deposits are rich where the side springs issued from cross fissures and furnished the ascending waters with ferrous sulphate. The gold is in the metallic form because reduced by the ferrous sulphate.

Organic material is capable of precipitating gold from its solutions. At many places the precipitation of the gold has been ascribed, in part at least, to the influence of the organic matter. Rickard[d] calls attention to the frequent association of metallic gold with sedimentary rocks bearing organic matter in California, New Zealand, Australia, and Tasmania. The most remarkable case is the concentration of gold in veins where they cross strata of carbonaceous shale, called indicators. Says Don,[e] "Away from the indicator, the greater part of the vein quartz is absolutely barren; but at the intersection with the indicator large

[a] Lindgren, Waldemar, The gold-quartz veins of Nevada City and Grass Valley, California: Seventeenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1896, p. 181. See also Pl. V, p. 134.

[b] Lindgren, op. cit., pp. 121–123.

[c] Lindgren, cit., pp. 130–131, 260, 261.

[d] Rickard, T. A., The origin of the gold-bearing quartz of Bendigo Reefs: Trans. Am. Inst. Min. Eng., vol. 22, 1894, pp. 314–315. Rickard, T. A., The indicator veins of Ballarat, Australia: Eng. and Min. Jour., vol. 60, 1895, pp. 561–562.

[e] Don, J. R., The genesis of certain auriferous lodes: Trans. Am. Inst. Min. Eng., vol. 27, 1898, p. 569.

masses of gold (often more than 100 ounces in one piece) have been obtained, and the greater part of the gold extracted from this belt has come from those parts of the quartz veins near some one of the indicators." Furthermore, Rickard[a] describes experiments in which the black carbonaceous shale of Rico was placed in silver solutions and in solutions containing Cripple Creek gold ore. Both metallic silver and gold were abundantly precipitated upon the shale in a short time. In the instances above mentioned it can hardly be doubted that the organic material was an important or controlling factor in the reduction and precipitation of gold.

The argillite with which many of the gold ores of the Sierra Nevada are associated is carbonaceous,[b] but the chief influence of this carbonaceous material may have been to assist in the production of the *ous* salts which ultimately reached the trunk channels. But in some places, as for instance where the pyrite occurs in a carbonaceous argillite, but not in quartz,[c] the gold may have been precipitated directly by the carbonaceous material. But since the gold in the Sierra Nevada is mainly deposited in open fissures,[d] the suggestion already made of direct reduction of the major portion of the gold by *ous* salts, and especially ferrous sulphate, is thought to be the more plausible, although if the formation of the ferrous sulphate be due to carbonaceous material in the country rock, the precipitation is indirectly due to organic matter.

The sulphides of the base metals also precipitate gold from its solutions. Below the level of ground water the rocks most commonly associated with gold are the sulphides of the base metals. Thus gold occurs on a great scale associated with pyrite. Very often it is found also with sulphides of the other metals, especially copper. In such occurrences, where the sulphides are abundant, the gold is likely to be plentiful; where the sulphides are present in small quantity, the gold also is likely to be deficient. This relation is illustrated in both California and Australasia,[e]

[a] Rickard, T. A., The Enterprise mine, Rico, Colo.: Trans. Am. Inst. Min. Eng., vol. 26, 1897, pp. 978–979.

[b] Lindgren, Waldemar, The gold-quartz veins of Nevada City and Grass Valley, California: Seventeenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1896, p. 81.

[c] Lindgren, op. cit., p. 140, Pl. VIII.

[d] Lindgren, op. cit., p. 259.

[e] Lindgren, Waldemar, The gold-quartz veins of Nevada City and Grass Valley, California: Seventeenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1896, pp. 124–126. Don, J. R., The genesis of certain auriferous lodes: Trans. Am. Inst. Min. Eng., vol. 27, 1898, p. 567.

and suggests that the original solution and deposition of native gold and the sulphides are frequently connected; therefore it is reasonable to infer that the conditions which produced sulphides may also have resulted in the precipitation of gold.[a]

Liversidge has shown experimentally that pyrite, galena, arsenopyrite, and nearly all other sulphide minerals will precipitate gold completely from solutions of auric chloride.[b] The frequency with which gold occurs associated with or inclosed by pyrite suggests that this is a very important reaction. This relation is well illustrated by the gold-quartz veins of the Sierra Nevada described by Lindgren, where in the deeper parts of the lodes beyond the belt of surface oxidation the pyrite and the gold are intimately associated. Lindgren says that the intimate connection of the gold with the sulphides was very likely caused by the tendency of gold solutions to be precipitated by particles of sulphides.[c]

In certain cases gold occurs associated with both carbonaceous material and the base sulphides. This is well illustrated by the argillite of the gold-quartz veins of the Banner mine described by Lindgren,[d] and by the Bendigo reefs of Australia.[e] In such cases the question may arise as to which of the two is the precipitating agent; but the more intimate association of the gold with the pyrite suggests that the pyrite is the precipitating agent for the gold (see Pl. XI, *A*), and this agrees with the experimental work of Liversidge, which shows that the metallic sulphides precipitate gold from solutions more readily than organic matter.[f]

Recently Lenher and Hall[g] have shown that the natural tellurides of gold, silver, and mercury are capable of rapidly and completely precipitating metallic gold from its solutions. This they have accomplished with calaverite ($AuAgTe_2$; Au 39.5, Ag 3.1, Te 57.4) (Au 41.76, Ag .80, Te 56.64,

[a] Lindgren, cit., p. 184.

[b] Lindgren, Waldemar, Gold-quartz veins of Nevada City and Grass Valley: Seventeenth Ann. Rept. U. S. Geol. Survey, pt 2, 1896, p. 182. Liversidge, A., On the origin of gold nuggets: Proc. Roy. Soc. New South Wales, vol., 27, 1893, p. 303.

[c] Lindgren, cit., p. 184, Pl. VII, p. 138, and Pl. VIII, p. 140.

[d] Lindgren, cit., Pl. VIII, fig. c, p. 140, and p. 156.

[e] Rickard, T. A., Origin of gold-bearing quartz of Bendigo reefs, Australia: Trans. Am. Inst. Min. Eng., vol. 22, 1894, pp. 314–317.

[f] Liversidge, A., On the origin of moss gold: Proc. Roy. Soc. New South Wales, vol. 27, 1893, p. 287.

[g] Lenher, Victor, Naturally occurring telluride of gold: Jour. Am. Chem. Soc., vol. 24, 1902, pp. 355–360. Lenher, Victor, and Hall, R. D., Action of tellurium and selenium on gold and silver salts: Ibid., pp. 918–927.

from Kalgoorlie),[a] krennerite ($AuAgTe_2$; Au 35.5, Ag 19.4, Te 45.1, uncertain), sylvanite ($AuAgTe_2$; Au 24.5, Ag 13.4, Te 62.1), hessite (Ag_2Te), kalgoorlite ($HgAu_2Ag_6Te_1$), nagyagite ($Au_2Pb_{14}Sb_3Te_7S_{17}$), and coloradoite (HgTe). It thus appears that whether these minerals are largely tellurides of gold, as calaverite; of gold and silver, as krennerite, sylvanite, etc.; of silver, as hessite, or of mercury, as coloradoite, when brought into contact with chloride of gold solutions metallic gold is precipitated. This experimental work of Lenher and Hall is of very great importance, probably largely explaining the intimate association of free gold with the tellurides at various places.

It will be explained (pp. 1170–1171) that in many places the association of free gold with tellurides is partly due to the reconcentrating action of descending water, the tellurides being the precipitating agent. Doubtless in many cases this process of reconcentration is also combined with that of direct oxidation of the tellurium of the tellurides, leaving gold behind. The spongy gold pseudomorphous after telluride, such as that which occurs at Cripple Creek, is almost certain evidence of one or both of the above processes. But in many cases the free gold associated with tellurides may be due to a first precipitation from ascending waters, the precipitating agent being the telluride. This possibility is illustrated by the Kalgoorlie district of Australia, described by Bancroft, who says: "The ore is very slightly altered country rock containing iron pyrites and tellurides of gold. . . . One of the interesting phenomena of the ore is the occurrence, once in a while, of small particles of crystalline gold surrounded by crystals of tellurides low in gold."[b]

The conclusion that the Kalgoorlie gold may be precipitated by the tellurides is confirmed by observations made by Rickard. He states that "free gold at Cripple Creek has invariably that appearance which characterizes the metal when it has originated from the disintegration of tellurides; but at Kalgoorlie ordinary gold, in a bright and crystalline condition, also occurs."[c]

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[a] Rickard, T. A., The telluride ores of Cripple Creek and Kalgoorlie: Trans. Am. Inst. Min. Eng., vol. 30, 1901, p. 711.

[b] Bancroft, Geo. J., Kalgoorlie, Western Australia, and its surroundings: Trans. Am. Inst. Min. Eng., vol. 28, 1899, pp. 93–94.

[c] Rickard, T. A., Telluride ores of Cripple Creek and Kalgoorlie: Trans. Am. Inst. Min. Eng., vol. 30, 1901, p. 714.

Bearing in the same direction are facts given by Kemp: "From Mr. Bancroft the writer learns that the actual ore at Kalgoorlie consists of calaverite and native gold. In a specimen kindly given the writer there is a yellow telluride and a silvery one. In the midst of the latter a bit of wire gold is embedded. There is no sign of alteration, and the native metal and the telluride must have crystallized together."[a]

The very general occurrence of tellurides in gold deposits leads me to the belief that the precipitation of gold by tellurides is probably an important reaction in the first concentration by ascending waters. The work of Hall and Lenher shows conclusively that where gold-bearing solutions enter deposits containing tellurides, whatever their origin, the gold will be rapidly precipitated by the tellurides. In this connection the manner in which the tellurium travels and is precipitated is important, and is discussed with the tellurides. (See pp. 1119–1125.)

Hall and Lenher[b] have shown that silver selenide also reduces gold to the metallic form almost as rapidly as selenium does. The reaction takes place only slightly in the cold, but readily on warming. Whether or not this has any importance with reference to ore deposits is uncertain.

In many cases the precipitation of gold is not produced by a single one of the causes given, but by some combination of them. For instance, it has already been pointed out that the abundance of *ous* solutions and diminishing temperature work together. Again, the reducing action of organic material and that of base sulphides or tellurides, or both, may work together. In still other cases all of the above favorable conditions may occur simultaneously. The combination of organic matter with sulphides or tellurides is believed to be very common.

Such a combination is probably illustrated by the deposits of New South Wales, in which the gold is associated both with organic matter and with pyrite. In this case the organic matter was probably the chief agent in precipitating the base sulphides from the sulphates. In consequence of this reaction there are two compounds present capable of precipitating the gold, both the pyrite and the carbonaceous material. Since the work of Liversidge shows that the sulphides precipitate gold more readily than

[a] Kemp, J. F., Geological occurrence and associates of the telluride gold ores: Mineral Industry, 1898, p. 319.

[b] Hall and Lenher, Action of tellurium and selenium on gold and silver salts: Jour. Am. Chem. Soc., vol. 24, 1902, p. 927.

organic material, and since the gold is more intimately associated with the sulphides, it seems probable that, in proportion to its mass, pyrite is a more important precipitating agent than the organic matter; but undoubtedly both are effective.

In many cases it is probable that the precipitation is due fundamentally to carbonaceous material, but that the influence of the organic matter is one step removed. That is to say, the organic matter first precipitated the baser sulphides by reducing them from sulphates, as explained under the succeeding section, and then the base sulphides precipitated the gold. This would seem to be the natural explanation which accounts for the close connection of the gold of some deposits with both carbonaceous materials and pyrite and other base sulphides.[a]

SILVER.

Metallic silver as a product of the first concentration by ascending waters is not an abundant source of the metal. One of the most notable occurrences of metallic silver of this origin is that of the Keweenawan of Lake Superior, where the silver, in subordinate amounts, is closely associated with copper.

Solution.—The form in which silver most extensively occurs is sulphide. It is well known that oxidizing waters change silver sulphide to a sulphate which is a readily soluble compound. It is therefore probable that the silver is very largely transported as a sulphate. It is also certain that silver is transported as a chloride, which may be produced either by the direct action of the chlorides or of hydrochloric acid on the sulphides of the metal, or by the interaction of the chlorides and sulphates. Silver carbonate is also somewhat readily soluble in carbonated solutions. Silver also occurs as a metal. It is well known that metallic silver is soluble in ferric sulphate, the reaction being:

$$2Ag+Fe_2(SO_4)_3=Ag_2SO_4+2FeSO_4$$

This reaction takes place in proportion as the ferric sulphate is abundant, and it has already been pointed out that such sulphates are likely to be abundant in the early part of the journey of the underground waters where they are descending. Stokes has shown that after this reaction has

[a] Don, J. R., The genesis of certain auriferous lodes: Trans. Am. Inst. Min. Eng., vol. 27, 1898, pp. 569, 612.

extended to equilibrium it will continue farther where the temperature is rising, and thus descending solutions with increasing temperature are favorable to solution of metallic silver. Doubtless silver is soluble to some extent in all the strong acids which occur underground and also in their salts. When, however, the silver becomes a salt, the form in which it would subsequently travel depends on the amount of acids in the solutions and their strength. It is well known that silver sulphide is soluble in alkaline carbonates and in hydrosulphuric acid, but probably silver thus transported is not an important source of metallic silver of the first concentration by ascending waters. From such compounds the silver is likely to be thrown down as a sulphide.

Precipitation.—The precipitation of silver in the metallic form from its solutions follows to a certain extent the same lines as that of gold; but silver is not nearly so readily reducible as gold, and therefore is not thrown down in the metallic form by so many compounds Silver is precipitated by metallic iron, by metallic copper, by cuprous compounds, readily by ferrous sulphate, and probably slowly by all other ferrous compounds. Of the *ous* salts, ferrous sulphate is doubtless the most important. The precipitation of the silver by ferrous sulphate is commonly written—

$$Ag_2SO_4 + 2FeSO_4 = 2Ag + Fe_2(SO_4)_3$$

The reduction is a function of the abundance of the reducing agent. Where the ferrous sulphate is abundant, and the temperature moderate it is believed that the more probable reaction for the precipitation of silver from its solutions is represented by the following equation:

$$Ag_2SO_4 + 3FeSO_4 + 4H_2O = 2Ag + Fe_3O_4 + 4H_2SO_4$$

Since ferric sulphate will dissolve silver, and ferrous sulphate will reduce silver, the relations of these two compounds are, as Stokes notes, reversible according to the following expression:

$$2Ag + Fe_2(SO_4)_3 \rightleftarrows Ag_2SO_4 + 2FeSO_4$$

Stokes says that the reaction moves in the direction of solution when the temperature is rising, and in the direction of precipitation when the temperature is falling. Thus, in ascending solutions, where the temperature is falling, silver is especially likely to be thrown down by the ferrous salts.

Silver may be also precipitated by ferrous compounds in a solid form, as in magnetite and the silicates. That this is certain follows from the fact

that such compounds are capable of reducing copper to a metallic condition from its solutions, and this element is more difficult to reduce than silver. That such reduction has actually taken place by the ferrous iron of silicates has been maintained by Vogt for the native silver at Kongsberg, Norway.[a]

COPPER.

Solution.—Copper in underground solutions is doubtless carried in many forms, probably more largely as copper sulphate, but as a chloride to an important extent. It may be transported also as copper carbonate in carbonate solutions carrying excess of carbonic acid. Copper as a sulphide is soluble in the alkaline sulphides, especially acid sodium sulphide (NaHS), and is soluble in considerable quantity in alkali sulpharsenates and sulphantimonates.

Precipitation.—Copper as a metallic compound is precipitated by metallic iron and by ferrous compounds. The precipitation by metallic iron is probably unimportant, but that by ferrous compounds is of great consequence. Copper occurs most extensively in the metallic form as precipitate of a first concentration in the Lake Superior region. Many years ago Pumpelly[b] noted the fact that in this region there is an intimate connection between the native copper and the iron-bearing minerals carrying ferrous iron. On this subject Pumpelly says:

> Throughout its deposits the copper exhibits a decidedly intimate connection with delessite, epidote, and green-earth silicates, containing a considerable percentage of peroxide of iron as a more or less essential constituent; while among the other silicates, viz, analcite, laumontite, datolite, prehnite, only the last named, which alone seems subject to a considerable replacement of its alumina by ferric oxide, is especially favored by copper. This association is so invariable * * * that there exists a close genetic relation between the metallic state of the copper and the ferric condition of the iron oxide in the associated silicates; that the higher oxidation of the iron was effected through the reduction of the oxide of copper and at the expense of the oxygen of the latter.[c]
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> * * * * * * *
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> Now, may we not consider the presence of iron in prehnite generally to be due to a beginning change, and the deposition of native copper in the Lake Superior prehnites to be partially or wholly correlated with the higher oxidation of the iron?[d]

[a] Vogt, J. H. L., Ueber die Bildung des gediegenen Silbers, etc.: Zeitschr. f. prak. Geol., April, 1899, p. 118.

[b] Pumpelly, Raphael, The paragenesis and derivation of copper and its associates on Lake Superior: Am. Jour. Sci., 3d series, vol. 2, 1871, pp. 353–354.

[c] Pumpelly, cit., p. 353.

[d] Pumpelly, cit., p. 354.

These observations of Pumpelly convinced me some years ago that the copper was reduced by the ferrous compounds. These conclusions have been later confirmed by experimental work. Biddle, in a thick-walled flask, reduced both cupric and cuprous chlorides by ferrous chloride in a saturated solution of potassium bicarbonate.[a] More recently Stokes, by heating an acidified solution of cupric sulphate and ferrous sulphate in a closed tube, has produced metallic copper at the cold end of the tube and pure hematite at the hot end of the tube. The reactions involved are as follows:[b]

$$2CuSO_4 + 2FeSO_4 \rightleftarrows Cu_2SO_4 + Fe_2(SO_4)_3$$

The Cu_2SO_4 is decomposed on cooling to Cu and $CuSO_4$, while $Fe_2(SO_4)_3$ decomposes on heating, thus:

$$Fe_2(SO_4)_3 + 3H_2O = Fe_2O_3 + 3H_2SO_4$$

Stokes further was able to reduce cupric sulphate to metallic copper by heating with hornblende in a closed tube to a temperature of 200° C. The reduction of the copper he attributes to the ferrous iron silicate of the hornblende. Thus experimental work completely confirms the conclusion that under natural conditions copper may be reduced from its salts by ferrous compounds, and that the metallic copper of the Lake Superior region was probably reduced both by ferrous solutions and by the ferrous iron of the solid compounds.

In the reactions written above it is supposed that where the copper salts are reduced by ferrous salts, ferric sulphate or hematite is produced. However, this is not necessary, nor where the ferrous salts are in excess is it believed to be probable that these are the common reactions. The natural reaction under such circumstances would be to produce magnetite, a compound not oxidized to the extent of ferric salts. The reaction may be represented as follows:

$$CuSO_4 + 3FeSO_4 + 4H_2O = Cu + Fe_3O_4 + 4H_2SO_4$$

By this reaction three molecules of the ferrous salts are required to produce one molecule of metallic copper, whereas if ferric salts be produced only two molecules of ferrous compound are needed. It is needless

[a] Biddle, H. C., The deposition of copper by solutions of ferrous salts: Jour. Geol., vol. 9, 1901, pp. 430–436.

[b] Stokes, manuscript.

to say that where the ferrous salts are very abundant well-known chemical principles lead to the conclusion that a partial oxidation of the ferrous compound is far more probable, since by the reduction of the copper an amount of oxygen is liberated sufficient to transform only a small part of the iron to the ferric state. In this connection it is to be remarked that in the Lake Superior native copper deposits ferrous compounds are very abundant, and magnetite is a very common mineral, both in the amygdaloid and conglomerate deposits. For example, Irving illustrates the intimate association of the native copper and the magnetite in the cupriferous sandstones of the Nonesuch mine, the copper frequently surrounding grains of magnetite.[a] My first interpretation of this relation was that the magnetite was probably the reducing agent which threw down the copper, but if this were so it should be transformed to hematite. My present view is that the native copper and the magnetite were both precipitated as a result of the reaction of ferrous salts upon copper salts. According to Stokes's work these would not be simultaneously precipitated at the same place. The magnetite would form where the temperature is higher and the copper where the temperature is lower. To explain the existence of both at the same place one is obliged to suppose that the magnetite formed first, and that later when the temperature was lower the copper was thrown down. It is notable that in the illustrative case mentioned, the copper does surround the grains of magnetite, and thus corresponds with Stokes's experimental work.

It is hardly necessary to say that in one district the chief reaction precipitating the copper may produce ferric salt and in another district may produce magnetite, while in still other districts the precipitation of the copper may be due to the combination of both reactions.

The Lake Superior copper deposits are believed to be an ideal case of ores deposited by ascending waters, the sources of which are the igneous rocks of the Keweenawan. In this region the only locality at which the ore has been found in paying quantities is at Keweenaw Point, and the productive district is at present confined to a very small area about Calumet and Houghton. Notwithstanding this fact, there is scarcely a locality in the Lake Superior region where the Keweenawan basic lavas occur in

[a] Irving, R. D., The copper-bearing rocks of Lake Superior: Mon. U. S. Geol. Survey, vol. 5, 1883, fig. 1, Pl. XVI, p. 127. (Description of same pp. 131–132.)

which small amounts of copper are not found. Almost every porous amygdaloid shows flakes of it. In many localities it is so abundant that extensive exploration has been undertaken, with the hope of finding large ore bodies, as, for instance, in Douglas County, Wis., Isle Royale, and Mamainse. But all of these explorations have resulted in failure. To me the almost universal association of small quantities of copper with the Keweenawan lavas is the most conclusive evidence that these lavas are the source of the metal.

While copper commonly occurs in many of the igneous rocks in its native state, especially in those which are porous, it is found in the less porous and therefore less altered rocks in minute quantities in the form of a sulphide, and this is thought to be the original form of the metal. That is to say, at the time the lavas crystallized the copper separated as copper sulphide or copper-iron sulphide. When the lavas were upturned by the formation of the Lake Superior syncline, and denudation began truncating them, the segregation of the copper deposits was inaugurated. The descending oxidizing waters transformed the copper sulphides into copper sulphates and took them into solution. The underground water was finally converged into trunk channels, and there met solutions bearing ferrous salts or came into contact with ferrous compounds. At such places reduction and precipitation took place. Where there were good trunk channels, as in the upper surfaces of many of the amygdaloids, there was sufficient segregration to encourage widespread exploration, as has already been noted. But only a few of the amygdaloids were open and scoriaceous enough to become the centering points of a sufficiently extended circulation to produce workable ore deposits. The greatest trunk channels were in the conglomerates. Where these conglomerates were interstratified with abundant lavas bearing a sufficient amount of copper, and there existed other necessary favorable conditions, the rising circulation has fortunately segregated the metal in great quantity. The most notable of these deposits is in the conglomerate upon which the Calumet and Hecla and the Tamarack mines are located.

SULPHIDES.

It has been stated that metals which occur as sulphides comprise iron, copper, lead, zinc, nickel, arsenic, antimony, mercury, and silver. Of these sulphides iron is the most abundant. Indeed, the sulphides of iron—

pyrite, marcasite, pyrrhotite, and other forms—exceed in quantity many fold all other sulphides. Standing next in amount is the group of zinc, lead, and copper sulphides, the order of abundance probably being that named. Nickel, arsenic, and antimony sulphides, also occur in important amounts. Mercury and silver sulphides, while important ores of these metals, are insignificant as compared with those previously mentioned so far as absolute quantity is concerned. As to the original source of the sulphides, it is well known that sulphide of iron occurs as an original constituent of igneous rocks. Probably the same is true of the other sulphides, but as their quantity is very much less they have been little noticed. Even if sulphides had not been observed to be original constituents of the igneous rocks, the large amount of sulphur compounds issuing from the interior of the earth, in connection with volcanism, would lead to the conclusion that sulphides must exist in the igneous rocks. This makes it highly probable that sulphur as sulphide is or was present in sufficient quantity in the original rocks to fully account for all of the sulphur compounds of the ore deposits.

While it is doubtless true that the original sources of all the sulphide ores are the sulphides of the igneous rocks, it does not follow that the igneous rocks are the immediate source of existing sulphide deposits. Indeed, in many instances this is not the case. For instance, it will be seen (p. 1146) that the sulphides of the lead and zinc deposits of the Mississippi Valley are segregated from sulphides in limestones. These sulphides were derived from the sulphides of earlier rocks which were probably transformed to sulphates, transported to the sea, and in the sea, as shown by Chamberlin, precipitated as sulphides at the same time the limestone was formed. In other cases, the sulphides of a particular ore deposit may be derived from a metamorphic rock. In many instances the sulphides of an ore deposit have their immediate source very largely in sulphides which have undergone one or more cycles of segregation by the processes which are given below. In many cases the sulphides of a given ore deposit are not derived from any single source or rock, but from the various sulphides in all the rocks through which the particular system of underground circulation producing the ore deposit passed.

SOLUTION OF SULPHIDES.

It is well known that the sulphides of copper, mercury, iron, nickel, lead, zinc, arsenic, and antimony are soluble in alkaline sulphides. Illustrating this general statement, Becker[a] has shown experimentally that the natural sulphide of mercury, cinnabar, the natural sulphide of iron, pyrite, the sulphide of copper, and the sulphide of zinc are soluble in sodic sulphide. Along the same line as Becker's work Doelter has shown that pyrite, stibnite, sphalerite, arsenopyrite, chalcopyryite, bournonite, and galena are all soluble in sodic sulphide.[b]

Becker has further shown that the sulphides of iron, copper, zinc, arsenic, and antimony are also soluble in alkaline carbonates containing, but not saturated with, hydrosulphuric acid.[c] This is partly equivalent to saying that they are soluble in sodium sulphide; for if hydrogen sulphide be introduced in sodium-carbonate solution, the following reaction immediately takes place:

$$Na_2CO_3+H_2S=Na_2S+H_2O+CO_2$$

But the observation by Becker is important, since it gives a method by which sodium sulphide, a solvent for the sulphides of the heavy metals, may be produced. In this connection it should be recalled that the carbonates of the alkalies are among the most abundant compounds carried by underground solutions, and hydrogen sulphide is known to be very common in such solutions. Therefore it is certain that considerable quantities of sodium sulphide will be produced where these two classes of solutions come together, as they are often sure to do. The formation of sodium sulphide in consequence of the mixture of sodium carbonate and hydrogen sulphide is probably of great importance in the genesis of ores.

Confirming the conclusions of Becker and Doelter, observation has shown that at Steamboat Springs, Nevada, and Sulphur Bank, California, mercuric sulphide and iron sulphide are transported in solutions containing sodic sulphide, hydrogen sulphide, sodium carbonate, and carbon dioxide.

[a] Becker, G. F., Quicksilver deposits of the Pacific coast: Mon. U. S. Geol. Survey, vol. 13, 1888, pp. 428-435.

[b] Doelter, C., Einige Versuche über die Löslichkeit der Mineralien: Tschermaks Mineral. Mittheil., Bd. XI, 1890, pp. 323-324.

[c] Becker, cit., pp. 432–435.

At Sulphur Bank boric acid is also present.[a] Hydrogen sulphide has also been observed by Lindgren in the ascending waters of the Federal Loan mine of the Sierra Nevada. He says that at the Federal Loan mine "an unmistakable odor of sulphureted hydrogen was noted in the vicinity of the spring."[b]

Finally, Doelter has shown that the sulphides are soluble in pure water, to some extent. He has thus dissolved measureable quantities of pyrite, galena, stibnite, sphalerite, chalcopyrite, arsenopyrite, and bournonite.[c]

Since sodic carbonate, sodic sulphide, and hydrogen sulphide are probably so important in the transportation of the sulphides of the metals, it is advisable to consider the possible sources of these compounds. This subject is of further importance, because it will be seen that hydrogen sulphide is also an important precipitating agent.

It has been fully explained in other places (pp. 176–177, 609–610, 677–679) that carbon dioxide is liberated on a great scale in the zone of anamorphism, and that most of this carbon dioxide joins the deep circulation. It has been seen also that the process of carbonation of the silicates is perhaps the most fundamental reaction of the zone of katamorphism—that in which aqueous ore deposits occur. Of the elements which the silicates contain, the most easily carbonated is sodium. It should follow that sodium carbonate is an abundant salt in the ground water. This theoretical conclusion is fully confirmed by observation.

We shall now see that abundant sodium carbonate results in the formation of the other compound most frequently present where sulphides of the valuable metals are in solution.

Stokes has shown recently that by the reaction of sodic carbonate alone upon pyrite or marcasite sodic sulphide is produced. His reaction is as follows:

$$8FeS_2+15Na_2CO_3=4Fe_2O_3+14Na_2S+Na_2S_2O_3+15CO_2$$

[a] Le Conte, Joseph, and Rising, W. B., The phenomena of metalliferous vein formation now in progress at Sulphur Bank, California: Am. Jour. Sci., 3d ser., vol. 24, 1882, pp. 23–33. Le Conte, Joseph, On the mineral vein formation now in progress at Steamboat Springs, compared with the same at Sulphur Bank: Am. Jour. Sci., 3d ser., vol. 25, 1883, pp. 424–428.

[b] Lindgren, Waldemar, The gold-quartz veins of Nevada City and Grass Valley districts, California: Seventeenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1896, pp. 121–122.

[c] Doelter, cit., pp. 321–323.

It is therefore evident that, since iron sulphide is the most common of the sulphides in nature and sodium carbonate an abundant carbonate, the reaction given is likely to take place on a considerable scale, and therefore that sodic sulphide, which is available to dissolve the sulphides of the other metals, is probably produced under natural conditions in large quantities.

Since experiment has shown the solubility of the sulphides in sodium sulphide and sodium carbonate, and observation has shown the frequent presence of these compounds, especially sodium carbonate, in underground water, there can be little doubt that the sulphides as such are transported on an extensive scale in the ground waters.

While the sulphides are somewhat readily soluble by various compounds, it is not believed that the material of the sulphide ores is carried to the openings in the rocks to be deposited by the ascending waters in the form of sulphide only. It has been fully explained that the sulphides in the belt of weathering are largely oxidized to sulphites and to sulphates, mainly the latter, and taken into solution by the descending waters. In this connection it is to be noted that the sulphates of iron, copper, zinc, nickel, mercury, and silver are all readily soluble; and even the sulphate of lead is dissolved to the extent of one part in 31,500 parts of water at 15° C.,[a] which is probably entirely adequate for the purposes of underground transportation. While the sulphur compounds of these metals are very largely transported as sulphates, they may also to some extent be transported as sulphites. Of these metals the sulphites of iron, copper, zinc, and silver are rather readily soluble.

PRECIPITATION OF SULPHIDES.

We have now seen that the metals which may be deposited as sulphides in the ore bodies may be transported as sulphides in solution or as sulphates. The question now arises as to the conditions which will result in their precipitation. It will be necessary to consider separately the precipitation of compounds transported as sulphides and as sulphates.

The more important metals which are known to be precipitated as sulphides in sufficient quantities to constitute ore are those of iron, lead, zinc, nickel, cobalt, copper, silver, mercury, arsenic, and antimony. As to

[a] Comey, A. M., Dictionary of Chemical Solubilities: London, 1896.

whether or not gold is also precipitated as a sulphide no definite statement can be made. The majority of those who have most closely studied gold deposits hold that the gold occurs either as free gold or as telluride. In evidence of this they cite the fact that where gold occurs with pyrite, as it so generally does, the microscopical study of the sulphides shows flakes of free gold within the sulphide. Admitting these facts, it does not at all follow that another portion of the gold is not present in the pyrite as a sulphide. Indeed, since gold sulphide is known to be a definite compound, which can easily be produced in the laboratory, and is produced by a metallurgical process, it seems to me highly probable that some of the gold is precipitated as a sulphide and in this form is associated with the sulphides of the other metals.

Precipitation of sulphides transported as such.—The precipitation of transported sulphides in the form in which they are found in the ore bodies may be accomplished either by simple dilution of the compounds, as pointed out by Becker[a] for mercury sulphide, by decreasing pressure and temperature, or by both. These are the conditions in ascending solutions, hence the transported sulphides are likely to be precipitated where the water is rising in trunk channels. The precipitation of the sulphides may result also from mingling of solutions. If, for instance, an acid, such as boric or sulphuric acid, be added to the solutions of the sulphides carried in alkaline carbonates and alkaline sulphides, the simple neutralization will result in the precipitation of many of the sulphides. By such neutralization the alkaline sulphide, the solvent, is destroyed. For instance, if sulphuric acid be added to a sodium sulphide solution the following reaction takes place:

$$Na_2S+H_2SO_4=Na_2SO_4+H_2S$$

This equation shows that not only is the solvent destroyed, but a precipitating agent for the sulphides is produced. Under such conditions, there can be no doubt that the sulphides will be rapidly precipitated. Also, where the sulphides are transported in solutions of sodium sulphide and sodium carbonate, the addition of hydrogen sulphide in excess will result in the precipitation of many of the metals.

[a] Becker, cit., pp. 429–431.

Very frequently the mingling of alkaline solutions of sulphides with acid solutions is at the points where descending and ascending waters meet. This is very well illustrated by the conditions at Steamboat Springs and Sulphur Bank, described by Le Conte,[a] where the surface descending waters are strongly acid, largely resulting from the oxidation of sulphides to sulphates, whereas the waters rising from the deep sources are strongly alkaline and bear sulphides in solution.

Precipitation of sulphides transported as oxidized salts.—Wherever below the level of ground water in the belt of cementation the sulphates and sulphites come in contact with buried organic material, or with solutions carrying organic compounds, the sulphates and sulphites may be reduced to sulphides. By such reduction ores may be directly produced. Where the salts of the metals are transported as sulphates the organic matter has merely to take away the oxygen of the sulphate in order to transform it to a sulphide. For instance, if the compound be lead sulphate ($PbSO_4$) the abstraction of the four atoms of oxygen produces galena (PbS). But in order that such compound be formed it is not necessary to suppose that the metals precipitated are transported as sulphates. It is only necessary to suppose that oxidized compounds of the metals and sulphates, with a reducing compound, are present. To illustrate, if silver be transported as a chloride with sodium sulphate in the solutions and oxygen be taken away from the sodium sulphate, this would be transformed to sodium sulphide, which would immediately precipitate the silver as silver sulphide. Again, supposing copper to be traveling mainly as carbonate, sodium sulphate to be present, and the reducing agent to be carbon, the end result is represented by the following reaction:

$$CuCO_3+Na_2SO_4+2C=CuS+Na_2CO_3+2CO_2$$

Of course the actual process would be as in the previous case. The compound containing the sulphur would be reduced to sulphide. This would react upon any of the compounds present which could produce insoluble sulphides.

Many ore deposits give evidence that the reducing action has been caused by organic material. Such cases are illustrated by disseminated sulphides occurring through carbonaceous material, as the graphite schist

[a] Le Conte, Joseph, Genesis of metalliferous veins: Am. Jour. Sci., 3d ser., vol. 26, 1883, p. 9.

of the Vermont copper mine described by Cazin.[a] The direct effect of the carbonaceous material in the production of the sulphides is also illustrated by the indicator veins of the Bendigo reef of Australia[b] and by the pyrite in the argillite described by Lindgren.[c] Another clear case of the direct reduction of oxidized salts by organic matter is that of the lead and zinc deposits of the Mississippi Valley. In Wisconsin, as shown by Blake,[d] lead and zinc are precipitated by the organic matter of the oil rock, and in Missouri, as shown by Bain,[e] by the organic matter of the Devonian shales. More frequently, however, the direct action of organic material upon the sulphates and sulphites is to form sparsely disseminated sulphides, which must be further worked over in order to produce ore deposits.

Recently Jenney has brought together a large number of instances in which there is a close association of ores with organic compounds, and these suggest that the organic material has directly or indirectly reduced sulphates to sulphides, and thus resulted in their precipitation.[f]

Probably sulphites and sulphates also may be reduced to sulphide by ferrous iron in the rocks. In the case of silver sulphate the reaction may be supposed to be as follows:

$$Ag_2SO_4+12FeSO_4+12H_2O=Ag_2S+4Fe_3O_4+12H_2SO_4$$

The reaction for the production of chalcocite from cuprous sulphate is:

$$Cu_2SO_4+12FeSO_4+12H_2O=Cu_2S+4Fe_3O_4+12H_2SO_4$$

and for cupric sulphate is:

$$2CuSO_4+15FeSO_4+16H_2O=Cu_2S+5Fe_3O_4+16H_2SO_4$$

It is to be noted that in these reactions magnetite is formed simultaneously with the production of the sulphides, and in order that the reactions

[a] Cazin, F. M. F., Discussion of genesis of ores: Trans. Am. Inst. Min. Eng., vol. 24, 1894, pp. 604–608.

[b] Rickard, T. A., The origin of the gold-bearing quartz of Bendigo reefs, Australia: Trans. Am. Inst. Min. Eng., vol. 22, 1894, p. 314.

[c] Lindgren, Waldemar, Gold-quartz veins of Nevada City and Grass Valley: Seventeenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1896, Pl. VIII, *C*, pp. 140, 156.

[d] Blake, Wm. P., Lead and zinc deposits of the Mississippi Valley: Trans. Am. Inst. Min. Eng., vol. 22, 1894, pp. 630–631.

[e] Bain, H. F., Van Hise, C. R., and Adams, Geo. I., Preliminary report on the lead and zinc deposits of the Ozark region: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, pp. 128–129.

[f] Jenney, W. P., The chemistry of ore deposition: Trans. Am. Inst. Min. Eng., vol. 33, 1903, pp. 445–448.

shall take place a very large amount of ferrous salt is necessary. Similar reactions may be written with the ferrous reducing salt in other forms than sulphate.

The class of reactions represented by the above equations has not been confirmed by experimental work in the laboratory. It was suggested by geological facts. In the basic volcanic rocks which have been profoundly altered by metasomatic changes in the belt of cementation secondary sulphides and magnetite are very generally present in close association. Such occurrences are very well illustrated by the ancient volcanics of the Lake Superior region—as, for instance, the Hemlock volcanic formation of the Crystal Falls district of Michigan.[a] For these rocks it can hardly be assumed that organic material or reducing agents other than the ferrous salts are present. But ferrous silicates, and, therefore, ferrous compounds, are very abundant; hence the suggestion that they are the agents which have resulted in the reprecipitation as sulphide of the sulphate compounds which have come down from the belt of weathering. The widely disseminated association of pyrite and magnetite in these rocks suggests that even the following reaction may possibly take place:

$$22FeSO_4+20H_2O=FeS_2+7Fe_3O_4+20H_2SO_4$$

If heat be liberated by this change, there is good chemical reason for its occurrence. But it must be admitted that this reaction is highly speculative and needs confirmation by experimental work.

At those places where the sulphates enter trunk channels, mingling of the solutions may cause precipitation when one of the solutions bears reducing agents. It is believed, however, that the precipitation of sulphates as sulphides in the trunk channels of circulation is far more frequently accomplished by hydrogen sulphide.

An important source of hydrogen sulphide is the reaction of organic matter upon the sulphides. Of such sulphides, that of iron is, of course, of the greatest consequence. Confirming the conclusion that the reaction of organic matter upon the sulphides may produce hydrogen sulphide is the fact that artesian waters held in sediments containing organic material are frequently marked by the presence of hydrosulphuric acid. This is

[a] Clements, J. Morgan, and Smyth, H. L., The Crystal Falls iron-bearing district of Michigan: Mon. U. S. Geol. Survey, vol. 36, 1899, pp. 73–154.

illustrated by the artesian waters of Wisconsin,[a] which are contained in a series comprising limestones and shales that are rich in organic matter. The influence of organic matter in producing hydrogen sulphide is further strongly suggested by the conditions at Sulphur Bank, where hydrogen sulphide is especially abundant in the solutions and the circulation of the ground water is through sedimentary rocks bearing abundant organic material.

Another source of hydrogen sulphide is the action of the dilute strong acids upon the sulphides. For instance, the reaction of sulphuric acid upon many of the base sulphides liberates hydrosulphuric acid.

Even the weak acid, carbonic, where abundant, produces hydrogen sulphide by reaction upon the alkaline sulphides, such as sodium sulphide. As already noted, Stokes has shown that the carbonates of the alkalies, by reaction upon the sulphides of the base metals, such as pyrite, form alkaline sulphides. If the sodium sulphide thus produced comes into contact with streams bearing carbonic acid, hydrogen sulphide will be produced. When it is remembered that in the solutions sodium carbonate is an abundant salt, that pyrite is the most plentiful sulphide, and that carbonic acid is the most abundant acid, it will be realized that the conditions must frequently arise which result in the production of hydrogen sulphide on a considerable scale.

Another way in which hydrogen sulphide can be formed is by the partial oxidation of the sulphides, especially the abundant iron bisulphide and pyrrhotite. On page 214 it was seen that the following reactions may take place:

$$3FeS_2+4H_2O+4O=Fe_3O_4+4H_2S+2SO_2$$
$$3Fe_{11}S_{12}+36H_2O+8O=11Fe_3O_4+36H_2S$$

The frequent association of magnetite with iron sulphide where the conditions have been favorable for partial oxidation suggests that this reaction may have taken place upon a considerable scale.

The hydrogen sulphide from any of the above sources may join the circulating waters bearing oxidized salts in solution and precipitate copper, zinc, lead, silver, and other metals as sulphides in the veins.

In this connection it is very interesting to note that Doelter, by treating metallic salts of the metals by hydrogen sulphide in somewhat dilute solu-

[a] Chamberlin, T. C., The ore deposits of southwestern Wisconsin: Geol. of Wisconsin, vol. 4, 1882, p. 547.

tions at temperatures of 100° or somewhat higher, has actually succeeded in producing artificially the following sulphide minerals: Pyrite, chalcopyrite, bornite, chalcocite, covellite, galena, bournonite, miargyrite, jamesonite, and pyrrhotite.[a]

Doubtless in many instances the precipitation of the oxidized salts is accomplished by an alkaline sulphide instead of by hydrogen sulphide. It has already been pointed out that the action of alkaline carbonates upon salts such as iron sulphide produces alkaline sulphides. For instance, sodium carbonate reacts upon iron sulphide, producing sodium sulphide. Where this sulphide comes into contact with any of the oxidized salts, or other soluble sulphates, the metals may be thrown down as sulphides.

A particularly good case of precipitation due to mingling of solutions is that of the lead and zinc deposits of the Missouri-Kansas district, described by Bain,[b] where waters rise through the Carboniferous limestone and come into contact with precipitating solutions derived from it. It is uncertain whether the precipitating solutions are alkaline sulphides, hydrogen sulphide, or reducing agents derived from organic matter, but probably hydrogen sulphide produced by reactions upon base sulphides is the more important precipitating agent.

Of the greatest importance in the precipitation of sulphides from ascending waters, the metals of which have been transported in the form of oxidized salts, is the reaction upon the solutions of previously precipitated sulphides. The sulphides of the less valuable but more abundant metals are important agents in the precipitation of the sulphides of the more valuable metals from the solutions of their oxidized salts. That such precipitation occurs was shown by Anthon in 1837.[c] In 1888 the same subject was investigated by Schürmann, whose results are but slightly different from those of Anthon. Schürmann[d] gives the following series of metals, the order being increasing strength of affinity for sulphur: Manganese, thallium, arsenic, iron, cobalt, nickel, zinc, lead, tin, antimony, cadmium, bismuth, copper, silver, mercury, palladium. He shows that the sulphide of the first mem-

[a] Tschermaks Min. u. Petrog. Mitth. vol. 7, 1886, p. 535 et seq.

[b] Bain, H. F., Van Hise, C. R., and Adams, G. I., Preliminary report on the lead and zinc deposits of the Ozark region: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, pp. 212–214.

[c] Anthon, E. F., Ueber die Anwendung der auf nassem wege dargestellten Schwefelmetalle bei der chemischen Analyse: Journ. f. Prak. Chemie, 1st series, vol. 10, 1837, p. 353.

[d] Schürmann, Liebig's Annalen der Chemie, vol. 249, 1888, p. 342.

ber of the series, manganese, reacts upon the oxidized salts of the following metals and precipitates them as sulphides, the precipitating agent at the same time going into solution as an oxidized salt. In a similar manner the sulphide of any other member reacts upon the oxidized salts of all the following members, precipitating the sulphides of them and going into solution as an oxidized salt. Thus the sulphide of iron is a precipitating agent for the oxidized solutions of zinc, lead, copper, and silver, throwing them down from their solutions as sulphides. Similarly the sulphides of copper throw down silver as sulphide from oxidized silver solutions. It is to be noted that the base metals, manganese, iron, and arsenic, as sulphides, are capable of precipitating practically all of the higher-priced metals; and that these compounds and zinc, lead, and copper sulphides are capable of precipitating silver. It is thus shown by experiment that the abundant sulphides of the baser metals are capable of precipitating, as sulphides, the more valuable metals from their oxidized salts.

In this connection the widespread occurrence of rhodochrosite and rhodonite in connection with ore deposits is very interesting. One or both of these minerals are found in almost every Western camp. They have been especially observed at the Butte and Little Belt Mountains districts of Montana, and the San Juan, Cripple Creek, Rico, and Aspen districts of Colorado. If manganese should be present in the veins as a sulphide, for instance, as alabandite (MnS), and oxidized solutions of any of the other metals come in, the sulphides of these other metals would be formed and the manganese would pass to the oxidized condition, and it is found as a carbonate or silicate in the deposits of the first concentration and frequently as a hydrated oxide in the deposits which have been affected by secondary alterations by descending waters. The oxidized manganese is precipitated as a carbonate or silicate because carbonic and silicic acids are the two abundant rock-making acids, and because these acids, with manganese, make insoluble compounds. When later the rhodochrosite and rhodonite in the belt of weathering are affected by secondary alterations, hydrated oxide of manganese, so prevalent in the upper parts of deposits, is produced. It at least is a suggestive coincidence that the rich gold streaks in the Camp Bird mine, Colorado,[a] are closely associated with impure

[a] Purington, C. W., Woods, T. H., and Doveton, G. D., The Camp Bird mine, Ouray, Colo.: Trans. Am. Inst. Min. Eng., vol. 33, 1903, p. 570.

rhodonite, and that in the Golden Fleece vein rhodochrosite "forms with quartz the gangue of the rich free gold ore."[a] At Rico also, according to Ransome, rhodochrosite "is important in these mines as a rough indication of good ore."[b]

Since manganese is not a very abundant metal, and since as a sulphide it has precedence over all other sulphides in its reactions upon oxidized salts of the other metals, being at the same time transformed to an oxidized product, it is natural to expect that manganese as rhodochrosite and rhodonite would be the dominating forms of manganese minerals in ore veins, and that manganese sulphide would be very rare, and such are the facts.

While manganese sulphide in many veins has doubtless been an important agent in the precipitation of ores of the first concentration by ascending water, it is probable that the much more abundant iron sulphide is of even greater importance in this connection. Just as oxidized salts of manganese are produced by the precipitation of the valuable metals by manganese sulphide, so the precipitation of such metals by iron sulphide produces oxidized salts of iron. Siderite is an even more important gangue in ores of the first concentration than rhodochrosite or rhodonite, thus indicating that the reaction suggested has taken place. Since, however, iron is so much more common than manganese, ordinarily not all of the iron sulphide has thus been oxidized, and hence in the veins pyrite is a very common gangue.

The reactions which caused the precipitation of the sulphides of the various metals from their oxidized solutions by the sulphides of other metals were not written out by Anthon and Schurmann, but recently Stokes has investigated the reaction in the case of iron sulphide with some of the solutions. Thus he has shown that pyrite and marcasite precipitate copper sulphide from cupric sulphate according to the following reaction:

$$5FeS_2+14CuSO_4+12H_2O=7Cu_2S+5FeSO_4+12H_2SO_4.$$

This reaction took place at 100° C. and above. Stokes has shown also that where sodium carbonate or potassium bicarbonate is present with the sulphide of iron and carbonates of various metals at 180° C., sulphides are

[a] Ransome, F. L., A report on the economic geology of the Silverton quadrangle, Colorado: Bull. U. S. Geol. Survey, No. 182, 1901, p. 73.

[b] Ransome, F. L., The ore deposit of the Rico Mountains, Colorado: Twenty-second Ann. Rept. U. S. Geol. Survey, part 2, 1901, p. 252.

precipitated in a different manner. For instance, in the case of lead carbonate with pyrite and marcasite, the reaction is as follows:

$$8FeS_2+14PbCO_3+Na_2CO_3=14PbS+4Fe_2O_3+Na_2S_2O_3+15CO_2$$

An interesting point in connection with this reaction is the production of hematite and sodium thiosulphate. Stokes shows also that zinc, copper, and silver are precipitated as sulphides by iron as sulphide in an analogous manner, the reactions being:

$$8FeS_2+15ZnCO_3+Na_2CO_3=15ZnS+4Fe_2O_3+Na_2SO_4+16CO_2$$

and

$$8FeS_2+15Ag_2CO_3+Na_2CO_3=15Ag_2S+4Fe_2O_3+Na_2SO_4+16CO_2.$$

While Stokes in the laboratory used temperatures of 100° C. and 180° C., it does not follow that the above reactions do not take place at lower temperatures but more slowly.

The above reactions in the presence of an alkaline carbonate are very suggestive, since they possibly explain in large part the association of lead, zinc, copper, and silver ores with limestone; for if calcium carbonate be substituted for sodium carbonate, similar reactions take place. It is not necessary to rewrite the equations, but the character of the reactions may be seen by substituting for Na_2CO_3 on the left-hand side the equations $CaCO_3$, and for $Na_2S_2O_3$ and Na_2SO_4 on the right-haud side the equation CaS_2O_3 and $CaSO_4$. Since these reactions are confirmed by experiment, we probably have the clue to the world-wide preference of many ores of lead, zinc, copper, and silver for the limestones. (See pp. 1086–1087.)

GENERAL STATEMENTS.

From the foregoing it appears that at the trunk channels of circulation the sulphur may enter in sulphides or in oxidized compounds in the forms of sulphites, sulphates, or other oxidized salts. If present as sulphides in alkaline solutions, the sulphides may be precipitated in consequence of the neutralization of the solution by an acid. They may be thrown down also in the ascending solutions in consequence of diminishing temperature and pressure. However, where the oxidized sulphur-bearing solutions reach trunk channels, as they frequently do, in order to precipitate the metals as sulphides they must become mingled with solutions bearing reducing agents, hydrogen sulphide, or alkaline sulphides, or must come into contact

with other sulphides previously precipitated or with other reducing agents. Any of these factors, or any combination of them, may cause the precipitation of the sulphides.

A case due to the combination of these factors is the precipitation of sulphides which later may react to precipitate the metal of the oxidized salts. For instance, in the early stage of the development of a deposit, the sulphides of iron and other base metals may be precipitated by hydrogen sulphide or some other compound, and later these previously precipitated sulphides take part in the precipitation of the sulphides of copper, silver, and mercury from the oxidized solutions of these compounds, such as sulphates.

While it is believed that sulphides are generally segregated in the first concentration by upward-moving waters, this is not supposed to be universal. Nature's processes are always too complex to be coverd by a single general statement. As a result of mingling solutions at various places, and of reactions between solutions and walls, many lateral-moving and downward-moving streams doubtless deposit rather than dissolve sulphides. Indeed, in the frequent case where in downward-moving waters sulphites or sulphates are reduced by organic matter to sulphides, precipitation of a portion of the sulphide is usual. Still the statement would hold true that upon the average more sulphides are dissolved than deposited by descending waters, and more sulphides are deposited than dissolved by ascending waters.

I conclude, therefore, that *sulphide ores, whatever their source, as first concentrates are generally deposited by ascending waters in the trunk channels.*

It appears that whether sulphur-bearing compounds reach trunk channels as sulphides or as oxidized salts, they are likely to be precipitated in such channels because solutions from various sources mingle there and come into contact with previously precipitated sulphides. The sulphides thus produced in the trunk channels may by denudation again reach the belt of weathering when the cycle is complete. These sulphides may be again oxidized to sulphate, and so on. It is therefore clear that sulphur, as sulphide and sulphate, may again and again take part in the deposition of ores,[a] but the first chief source of the sulphur is probably the sulphides of the original crystallized rocks and of magmas.

[a] Le Conte, Joseph, Genesis of metalliferous veins: Am. Jour. Sci., 3d ser., vol. 26, 1883, p. 13.

TELLURIDES.

The only important telluride ores are those of gold and silver. These compounds, until comparatively recently, were regarded as somewhat exceptional, and for the most part rather as mineralogical rarities than as ores. The earliest gold and silver tellurium ores to be mined were those of Nagyag, in Transylvania.[a] Gold mining in Colorado has added other and much more important localities where the tellurides are produced in important amounts. About 1872 the tellurides of Boulder County became of consequence. But of more importance than all of the previously known tellurides are those of Cripple Creek, Colorado, which began to be exploited in 1891.[b] Here the various tellurides are found, but the greater part of the gold is believed to occur in calaverite.[c]

Close mineralogical studies of ore deposits in recent years have shown that subordinate and usually unimportant amounts of tellurides, from an economic point of view, occur very generally associated with gold. Indeed, it appears that the presence of the tellurides with the gold ores of the first concentration is scarcely less prevalent than the association of pyrite with gold ores. The widespread occurrence of tellurides in connection with gold ores is illustrated by the Kalgoorlie district of West Australia, described by Bancroft;[d] by the Sierra Nevada gold deposits, described by Lindgren;[e] by the Judith Mountains and Little Rocky Mountains, Montana, described by Weed and Pirsson;[f] by the Potsdam gold ores of the Black Hills, described by Smith and Irving;[g] by the mines of Custer County, Colo., and by the Appalachian gold deposits, described by S. F. Emmons.[h]

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[a] Kemp, J. F., Geological occurrence and associates of the telluride gold ores: Mineral Industry, vol. 6, 1898, p. 295.

[b] Penrose, R. A. F., jr., Mining geology of the Cripple Creek district: Sixteenth Ann. Rept. U. S. Geol. Suvey, pt. 2, p. 118.

[c] Penrose, cit., p. 121.

[d] Bancroft, Geo. J., Kalgoorlie, Western Australia, and its surroundings: Trans. Am. Inst. Min. Eng., vol. 28, 1899, pp. 88–100.

[e] Lindgren, Waldemar, The gold-quartz veins of Nevada City and Grass Valley, California: Seventeenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1896, p. 117.

[f] Weed, W. H., and Pirsson, L. V., Geology and mineral resources of the Judith Mountains, Montana: Eighteenth Ann. Rept. U. S. Geol. Survey, pt. 3, 1898, pp. 589–592. Weed, W. H., and Pirsson, L. V., Geology of the Little Rocky Mountains, Montana: Jour. Geol., vol. 4, 1896, pp. 426–428.

[g] Smith, F. C., The Potsdam gold ores of the Black Hills of South Dakota: Trans. Am. Inst. Min. Eng., vol. 27, 1898, pp. 414–420. Irving, J. D., A contribution to the geology of the northern Black Hills: Annals New York Acad. Sci., vol. 11, 1899, pp. 297–311.

[h] Emmons, S. F., The mines of Custer County, Colorado: Seventeenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1896, p. 433. Emmons, S. F., Notes on the gold deposits of Montgomery County, Maryland: Trans. Am. Inst. Min. Eng., vol. 18, 1890, p. 407.

Since the tellurides are very generally associated with gold ores and the free gold deposited by the deep circulation is almost universally associated with pyrite and other sulphides, it follows that the tellurides deposited by the deep circulation are usually associated with sulphides. This is not only true of those localities in which the tellurides are unimportant as ores, but is equally true of the great telluride camps. Of Cripple Creek Penrose says: "The close association of tellurides with sulphides, especially iron pyrites, which themselves often carry gold, is also a point worthy of note. Not only are auriferous tellurium and sulphur compounds often thus mechanically associated in different minerals, but sometimes they replace each other in the same minerals, such as tetradymite, nagyagite, and tellur-sulphur." [a]

The tellurides are also very generally associated with fluorite, and Penrose notes that where the gold is mainly in sulphides fluorite has not often been observed.

It seems to me certain that the widespread association of the tellurides with gold and silver ores, especially with gold ores, has a genetic significance probably less important only than that of the base sulphides, especially iron sulphide. As to the source of the tellurium, nothing is positively known. In all of the above-mentioned districts in which tellurium is especially abundant, with the possible exception of the Kalgoorlie district, which has not yet been thoroughly studied and in which the age of the mineralizing dikes has not been established, are found comparatively recent igneous rocks, in which doubtless the tellurium largely had its origin. At first thought one might conclude that the gold, silver, and tellurium were transported as tellurides and deposited as such without chemical change, but the recent work of Lenher and Hall [b] is decidedly against this view. They have found no solvent whatever for tellurides of gold without breaking up these compounds and producing salts of tellurium, the gold usually being left in the metallic form. Moreover, as has already been noted, they have shown that metallic tellurium and seven of the more common mineral tellurides of gold and silver rapidly reduce gold from

[a] Penrose, R. A. F., jr., Mining geology of the Cripple Creek district, Colorado: Sixteenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1895, p. 157.

[b] Lenher, Victor, Naturally occurring telluride of gold: Jour. Am. Chem. Soc., vol. 24, 1902, pp. 355–360.

Hall, R. D., and Lenher, Victor, Action of tellurium and selenium on gold and silver salts: Ibid., pp. 918–927.

its solutions, forming metallic gold, the tellurium at the same time going into solution. Further, they have proved that the presence of any of the soluble tellurides, including hydrogen telluride, is sufficient not only to throw the gold out of solution, but to prevent it from getting into solution. Other soluble salts, where tellurium acts as an acid, are the tellurites and tellurates. Tellurous oxide or acid is also sparingly soluble. All of these compounds, like tellurides, precipitate gold from its solutions in a metallic form, not as telluride. From the foregoing it appears that if tellurium compounds in which tellurium is a part of the acid are essential for the formation of the tellurides of gold, these tellurium salts and the gold have come into the trunk channel from separate sources. They could not have traveled together; else the gold would have been thrown from the solutions before reaching the trunk channels.

It is to be remembered that tellurium, besides acting in an acid, also acts as a metal to the halogens (chlorine, bromine, and iodine). The telluric compounds of this class, such as telluric chloride ($TeCl_4$), being completely saturated, so far as tellurium is concerned, have no reducing power, and they may therefore travel with gold solutions. But the tellurous combinations with the halogens, such as tellurous chloride ($TeCl_2$), can not travel with gold, for Lenher has shown that such tellurous salts in the presence of water and its compounds react upon the water, producing metallic tellurium and telluric chloride according to the following equation:

$$2TeCl_2+H_2O=Te+TeCl_4+H_2O$$

The metallic tellurium would then reduce the gold, which would therefore be precipitated before reaching the trunk channels.

The almost invariable association of tellurides with sulphides, already noted, naturally leads to the suggestion that the same conditions were favorable to the deposition of the sulphides and the tellurides. In this connection the occurrence at Cripple Creek is especially interesting. Mr. Moore, consulting engineer of the Portland mine, informs me that in this district near the surface the values are found in the oxidized zone as native gold; that deeper, the values are mainly in the tellurides, the associated sulphides being very lean; and that still deeper the values are found both in the tellurides and in the sulphides of iron. The depth at which the sulphides at the Portland mine begin to have value is about 200 meters.

These facts strongly favor the precipitation of the gold as a first concentrate simultaneously in the sulphides and the tellurides. It is believed (see pp. 1172–1174) that the abundant native gold at the surface and in the tellurides at intermediate zones to the exclusion of the sulphides is due to secondary reaction by descending water.

It may be that the key to the problem of the deposition of the tellurides lies in their association with sulphides. We have already seen that telluric salts of the type of $TeCl_4$ may travel with gold in solutions. It has already been pointed out that gold, in most cases, probably also travels as a chloride, and thus solutions of auric chloride and telluric chloride may together enter trunk channels which contain sulphides. In such trunk channels the reaction of the sulphides might reduce both the gold and the tellurium simultaneously and thus produce tellurides of gold; or, by the reaction of the sulphides upon the telluric salts, these may be reduced to tellurous salts, which, as already explained, would decompose into metallic tellurium and telluric salts, and the tellurium would precipitate the gold. Under these or some other conditions, the gold and tellurium go down together, with a definite composition, and thus form the tellurides.

The invariable association of silver with the tellurides of gold suggests the possibility that the presence of silver salts is essential for the formation of the tellurides of gold. But in some cases the silver is very low in the tellurides, although rarely as low as 0.8, as in the case of one specimen of calaverite from Kalgoorlie,[a] which makes it improbable that the presence of silver salts is essential for the precipitation of the tellurides.

The association of the tellurides with fluorite has already been mentioned, and this association suggests a genetic relation between the two; but bearing in the opposite direction are the observations made by Penrose at Cripple Creek, where the abundance of fluorite has no definite relation to the abundance of tellurides.[b] Possibly pointing in the same direction is the experimental work of Lenher,[c] who has shown that gold and gold oxide are absolutely insoluble in hydrofluoric acid. Not only is this the case, but when any gold salt is brought into contact with a soluble fluoride the gold is immediately precipitated as a hydrate. This is true

[a] Rickard, T. A., Telluride ores of Cripple Creek and Kalgoorlie: Trans. Am. Inst. Min. Eng., vol. 30, 1901, p. 711.

[b] Penrose, cit., pp. 158–159.

[c] Lenher, Victor, Fluoride of gold: Jour. Am. Chem. Soc., vol. 25, 1903, pp. 1136–1138.

even for silver fluoride, which, according to Lenher, acts upon gold chloride as follows:

$$AuCl_3+3AgF+3H_2O=3AgCl+Au(OH)_3+3HF$$

Lenher's work suggests the advisability of experimenting as to the effect of the soluble fluorides and of hydrofluoric acid upon solutions bearing chlorides of both gold and tellurium. In this or some other combination of the three elements gold, tellurium, and fluorine with perhaps other compounds may lie the key to the problem of the precipitation of the gold tellurides.

The abundant fluorite associated with the tellurides has frequently been cited as evidence of pneumatolitic action in connection with such deposits. But Penrose's description of the Cripple Creek ores gives no support to this hypothesis. All his descriptions show the phenomena to be those which, in many other districts, are well known to be due to water solutions. For instance, the most abundant gangue mineral of the district is silica in quartzose, chalcedonic, and amorphous forms. It is well known that these compounds are the most abundant ones deposited by underground water. Others of the more abundant gangue minerals are oxides of manganese, calcite, gypsum, barite and kaolin.[a]

Furthermore, in some of the mines, as the Gold Coin mine, the ore of which is in granite, there has been solution of biotite, quartz, and feldspar, and this can not be attributed to pneumatolitic action.[b]

I therefore find no evidence of pneumatolitic action in connection with the genesis of the telluride ores. It is uncertain what conditions produce a somewhat homogeneous compound consisting of definite proportions of silver, gold, and tellurium, as in the telluride minerals. Doctor Lenher has been at work on this problem for some time, but as yet without determinative results. He has treated gold solutions with hydrogen telluride and has worked on the various tellurium compounds, such as the chloride, bromide, fluoride, and alkaline tellurites, all experiments being made in the presence of a reducing agent, such as sulphurous acid; yet in no case has he been able to get homogeneous compounds of gold and tellurium, but, on the contrary, has obtained metallic gold and tellurium salts, or mixtures of gold and tellurium of irrational composition. While the problems of the

[a] Penrose, cit., pp. 123-129.

[b] Penrose, R. A. F., jr., Mining geology of the Cripple Creek district: Sixteenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1895, pp. 159-161.

transportation of the compounds resulting in the tellurides and of the precipitation of the tellurides have not yet been solved, there is little doubt that careful chemical work will solve them.

In view of all the foregoing facts, the most plausible suggestion which I am able to make as to the development of the tellurides is as follows: The gold is taken into solution by descending waters in the early part of the journey in the form of a chloride, as explained on pages 1089–1091. The tellurium is widely dispersed, possibly to some extent as metallic tellurium, but more largely as a telluride, and is oxidized in the belt of weathering. It there unites with an acid and travels as a soluble salt, perhaps, also, in large part, as telluric chloride. That reactions of this kind take place with reference to the tellurides in the belt of weathering are certain, as shown by the abundant spongy gold at Cripple Creek, pseudomorphous after the various tellurides, showing that such reactions have taken place there on an extensive scale. The auric chlorides and telluric salts, such as telluric chloride, may travel together without reaction, or they may come together in the trunk channels. There they become mingled with reducing compounds in solution, or, as has been suggested, come into contact with reducing solids, such as the sulphides. It is believed the tellurium and gold are simultaneously reduced under such conditions that they unite in definite compositions, and thus produce the telluride minerals.

Hall and Lenher were more successful in the production of telluride of silver. An ammoniacal solution of silver chloride in contact with tellurium at room temperatures resulted in the production of silver telluride according to the following reaction:

$$4AgCl+3Te=2Ag_2Te+TeCl_4$$

When the nitrate of silver was used "a greater range of temperature was possible, and the solution was either boiled continuously or kept at a temperature of about 80° C. for a long time."[a] The reaction in this case as given by them is:

$$4AgNO_3+3Te=2Ag_2Te+Te(NO_3)_4$$

Since, however, it is difficult to understand how metallic tellurium can be carried in solution, there is a possibility that the silver tellurides are

[a] Hall, R. D., and Lenher, Victor, Action of tellurium and selenium on gold and silver salts: Jour. Am. Chem. Soc., vol. 24, 1902, p. 922.

produced in nature not by the reaction of metallic tellurium but by tellurous salts which, according to Lenher, precipitate silver by the following reactions:

(a) $2TeCl_2+H_2O=Te+TeCl_4+H_2O$
(b) $4AgNO_3+3Te=2Ag_2Te+Te(NO_3)_4$

While the reactions given may possibly explain the formation of a part of the silver telluride in the rare mineral hessite, it is to be remembered that pure silver telluride is very exceptional.

Commonly, so far as silver occurs with tellurium, it is in minerals in which there is also telluride of gold, and frequently telluride of lead, mercury, and antimony. It therefore follows that the conditions under which the telluride of silver is precipitated must be the same in most cases as those which cause the formation of the telluride of gold. Hence the solution of the problem of the precipitation of tellurides of gold will probably also be the solution of the problem of the precipitation of the telluride of silver.

OXIDES.

The oxide ores that are deposited by ascending water below the belt in which the effect of descending waters is evident are dominantly hematite (Fe_2O_3) and magnetite ($FeO \cdot Fe_2O_3$), and possibly zincite (ZnO), franklinite ($(FeZnMn)O \cdot (FeMn)_2O_3$), and cassiterite ($SnO_2$).

The association of hematite and magnetite with the sulphides of the first concentration far below the belt where oxidizing waters can act is so well known that it is not necessary to amplify by giving illustrations.

So far as I know the chief occurrences of zincite and franklinite in deep-seated deposits with no evidence of superficial oxidation are in New Jersey, especially at the famous localities of Franklin Furnace and Sterling.[a] It is notable that here magnetite also occurs associated with the zincite and franklinite. Magnetite associated with pyrite and marcasite occurs very extensively in the Lake Superior region, especially in Canada, although these minerals are found together on the south shore of Lake Superior, as at the Republic trough. The question at once arises whether the metals were transported to their present positions in solution and deposited by ascending waters, or, on the contrary, were produced by alterations of solid

[a] Kemp, J. F., The ore deposits of Franklin Furnace and Ogdensburg, New Jersey: Trans. New York Acad. Sci., vol. 13, 1893–94, pp. 76–96.

compounds in the zone of anamorphism by the processes of dehydration, decarbonation and deoxidation.

Magnetite.—The formation of magnetite in the zone of anamorphism is fully discussed on pages 845–846, and will not again be described here. The reactions producing magnetite are believed to be as follows:

$$3FeCO_3+O=Fe_3O_4+3CO_2$$
$$2FeCO_3+FeS_2+2H_2O=Fe_3O_4+2H_2S+2CO_2$$
$$3(Fe_2O_3 . nH_2O)-O=2Fe_3O_4+3nH_2O$$
$$22(Fe_2O_3 . nH_2O)+FeS_2+2H_2O=15Fe_3O_4+2H_2SO_4+22nH_2O$$

Zincite.—In order to produce zincite in the deep-seated zone from smithsonite, it is only necessary that the water and the carbon dioxide be driven off, thus:

$$ZnCO_3 . H_2O=ZnO+H_2O+CO_2$$

If smithsonite were formed in the belt of weathering, as explained on pages 1144–1145, 1147–1148, and later by burial transferred to the zone of anamorphism, the above reaction would almost certainly take place.

Franklinite.—In the case of franklinite it is necessary only to suppose that with the smithsonite there was a certain amount of hydrous oxide of iron and manganese. It is well known that the smithsonite produced in the belt of weathering almost universally contains hydrous oxide of iron. Not infrequently it is also associated with hydrous manganese oxide. If smithsonite, hydrous oxide of iron, and hydrous oxide of manganese be taken in the proper proportions, and subjected to dehydration, decarbonation, and deoxidation, franklinite may be produced. For simplicity suppose that the iron, zinc, and manganese in the resultant franklinite are equally abundant as ferrous oxide, and iron and manganese equally abundant as ferric oxide. The reaction may then be written as follows:

$$2(ZnCO_3 . H_2O)+4(Fe_2O_3 . 1\tfrac{1}{2}H_2O)+4(Mn_2O_3 . H_2O)-4O=$$
$$6[(FeZnMn)O . (FeMn)_2O_3]+12H_2O+2CO_2$$

Hematite.—It is well known that hematite occurs as a gangue mineral in connection with the sulphides in veins, although so far as I know there is no case in which such hematite occurs in sufficient amount to be called an ore. In this connection the recent work of Stokes is interesting.[a] He has shown that FeS_2 as pyrite and marcasite is a ferric iron; and further, that

[a] Stokes, H. N., On pyrite and marcasite: Bull. U. S. Geol. Survey No. 186, 1901, pp. 50.

from this ferric iron hematite can be produced by the action of certain carbonates and alkaline carbonates without oxidation. By reactions of zinc, lead, and silver carbonates with an excess of alkaline bicarbonate, he has produced hematite according to the following reactions:

$$8FeS_2+14ZnCO_3+Na_2CO_3=4Fe_2O_3+14ZnS+Na_2S_2O_3+15CO_2$$
$$8FeS_2+14PbCO_3+Na_2CO_3=4Fe_2O_3+14PbS+Na_2S_2O_3+15CO_2$$
$$8FeS_2+15Ag_2CO_3+Na_2CO_3=4Fe_2O_3+15Ag_2S+Na_2SO_4+16CO_2$$

He has also produced hematite from the sulphide through the reaction of the alkaline carbonate alone at temperatures of 100° C. and 190° C., thus:

$$8FeS_2+15Na_2CO_3\rightleftarrows 4Fe_2O_3+14Na_2S+Na_2S_2O_3+15CO_2$$

This last reaction is reversible, but Stokes remarks it will proceed to an end if the sulphide and thiosulphate be carried away, as by a circulating solution, or if there be present a metallic salt capable of precipitating the alkaline sulphide as fast as it is formed, as in the first three reactions above given.

Cassiterite.—In reference to cassiterite (SnO_2) Lindgren calls attention to the work of Winkler, Sandberger, and Verbeek, which shows that tin "may be held in solution and deposited at ordinary pressure by thermal waters."[a] However, in this connection it is to be remembered that both Vogt and Beck strongly insist that cassiterite is formed, to use the words of Vogt, "by eruptive after-action." Vogt says of the cassiterite veins that their "material contents were extracted from the not yet fully congealed granite."[b] Further, Vogt and Beck, if I understand them correctly, following Elie de Beaumont and Daubrée, regard the extraction from the "not yet fully congealed granite" as accomplished by pneumatolytic processes. Upon the point that tin ore may be thus formed I express no opinion.

I do not doubt that tin, like other metals, has been transported by underground waters, and from such solutions precipitated as cassiterite. As is well known, tin may be readily carried by water as the sulphate, nitrate, or chloride, and doubtless is also transported in other forms. From stannic solutions at ordinary temperatures hydrated stannic oxide is thrown down by the alkaline carbonates. It may be that at the relatively high

[a] Lindgren, Waldemar, Metasomatic processes in fissure veins: Trans. Am. Inst. Min. Eng., vol. 30, 1901, p. 625.

[b] Vogt, J. H. L., Problems in the geology of ore deposits: Trans. Am. Inst. Min. Eng., vol. 31, 1902, p. 135.

temperatures and pressures which exist in the deeper parts of fissure veins, this reagent would result in anhydrous stannic oxide, or cassiterite; but this is a mere suggestion. The conditions under which anhydrous stannic oxide is precipitated from its solutions should be experimentally investigated.

In conclusion it may be said that one oxide which very probably is deposited by ascending waters as an ore is cassiterite.

CARBONATES.

Aside from hydrosulphuric acid, the acid of great importance in the deposition of ores is carbonic acid. This, as is well known, is indeed the dominant acid contained in issuing underground waters. This point both Le Conte[a] and Posepny[b] strongly emphasize. I have already pointed out sources for the excess of carbon dioxide held in the underground waters. (See p. 678.)

A very interesting confirmation of the theory given on the pages referred to regarding the liberation of silica by the process of carbonation near the surface and the liberation of carbon dioxide probably by the process of silication at depth is furnished by the Geyser mine of Custer County, Colo., described by Emmons.[c] Here waters were analyzed from the 154-meter and the 615-meter levels. The surficial waters contain ten times as much silica as the deep-seated waters, and the deep waters hold a greater quantity of carbonic acid than the vadose circulation.

The carbonates which are most extensively deposited in the veins of the first concentration are those of calcium and magnesium as calcite ($CaCO_3$) and dolomite ($CaCO_3 . MgCO_3$). While calcite and dolomite are the dominant carbonates in the gangue, the carbonates of the other alkaline earths, strontianite ($SrCO_3$) and witherite ($BaCO_3$), are also well known. The other important carbonates are those of iron—siderite ($FeCO_3$)—and of manganese—rhodochrosite ($MnCO_3$). Of course, it is well known that carbonate of zinc (smithsonite) and carbonates of copper (azurite and malachite) occur abundantly as ores; but these are mainly secondary products of descending waters and do not come under the subject now being consid-

[a] Le Conte, Joseph, Genesis of metalliferous veins: Am. Jour. Sci., 3d ser., vol. 26, 1883, p. 11.

[b] Posepny, F., The genesis of ore deposits: Trans. Am. Inst. Min. Eng., vol. 23, 1894, p. 237.

[c] Emmons, S. F., The mines of Custer County, Colo.: Seventeenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1896, pp. 460–464.

ered, the deposits of a first concentration by ascending waters. It has been explained in various parts of this treatise that the two great rock-making acids are carbonic acid and silicic acid, and further it has just been explained that in the deep-seated zone carbonic acid is extensively produced. Thus it is entirely natural that so far as the metals are somewhat soluble and can travel as carbonates, they will do so. This applies especially to the alkalies and the alkaline earths, and to iron and manganese. When carbonate solutions containing these various metals rise in the trunk channels of circulation with diminishing temperature and pressure, it naturally follows that the less soluble of the carbonates are thrown down in large amounts. These less soluble carbonates are calcite, dolomite, siderite, and rhodochrosite. The carbonates of sodium and potassium are not thrown down, because these compounds are so readily soluble.

In conclusion it may be said that the carbonates, as original deposits by ascending waters, are essentially gangue minerals, not ores. So far as I know none of them are mined as ores within the United States, although in some places siderite and rhodochrosite, as deposits of the first concentration by ascending waters, may be an unimportant source of iron and manganese ores.

Excellent illustrations of rhodochrosite as a gangue mineral are furnished by the San Juan district, Colorado. This carbonate is generally found in that area, but is an especially important and abundant gangue mineral at the Smuggler Union mine.

SILICATES.

The silicates are well known to be important gangue minerals deposited by the deep circulation. If one were to give a list of the silicates which have been found as gangue in veins in various parts of the world, it would comprise a large proportion of the entire list of silicates. This is an inevitable consequence of the facts that, first, the dominant acid of nature is silicic acid, and second, the silicates for the most part are rather insoluble, many of them extremely so. It has been explained at various places that silica as colloidal silicic acid travels in great quantities through the rocks, being produced on an enormous scale in the belt of weathering by the process of carbonation. (See pp. 173–177, 480.) Silicic acid formed in this manner and released by other reactions thus enters the belt of cementation and finds its way to the trunk channels of circulation, to

which come also metals in various combination. Where silicic acid and the salts of the metals thus meet it is certain that the silicates form extensively, according to the law of mass action that the most abundant compounds are most likely to be precipitated, and in consequence of the law that the most insoluble compounds are likely to be thrown down.

Of the silicates in fissure veins Lindgren regards the following of sufficient importance to be cited: Muscovite, biotite, chlorite, pyroxene, amphibole, garnet, epidote, orthoclase, albite, tourmaline, topaz, kaolinite, and zeolites.[a]

Lindgren's description of the occurrence of these minerals shows that the hydrous silicates are dominant. While a considerable number of the anhydrous silicates form, they are very subordinate in amount. The significance of these facts is discussed on pages 1055–1060. The abundance and prevalence of the hydrous silicates are beautifully illustrated by the copper deposits of the Lake Superior region. Here there has been scarcely any discoverable effect of descending waters, as recent glacial erosion has entirely removed the belt of weathering of pre-Glacial time. Pumpelly gives the following list of hydrous silicates as occurring in this region: Analcite, apophyllite, chlorite, datolite, delessite, epidote, laumontite, prehnite.[b] This list has since been supplemented by Hubbard, the following being added: Chabazite, chlorastrolite, chrysocolla, harmotome, heulandite, lennhardite, mesotype, natrolite, pectolite, saponite, stilbite, thomsonite.[c] While in the Lake Superior copper deposits the dominance of the hydrous silicates is clear, the gangue minerals are not restricted to them, but comprise anhydrous minerals—orthoclase and wollastonite being mentioned.

It is to be noted that the silicate gangue minerals retain even some of the alkalies, i. e., sodium and potassium. Sodium is found in analcite, chabazite, chlorastrolite, mesotype, natrolite, pectolite, stilbite, and thomsonite; and potassium is found in apophyllite, chabazite, harmotome, and orthoclase. By the union of the alkalies with other bases and with silica it is possible to produce compounds insoluble in the liquids present, and where this could take place as demanded by the laws of chemistry, it has occurred,

[a] Lindgren, Waldemar, Metasomatic processes in fissure veins: Trans. Am. Inst. Min. Eng., vol. 30, 1901, pp. 607–615.

[b] Pumpelly, Raphael, The paragenesis and derivation of copper and its associates on Lake Superior: Am. Jour. Sci., 3d series, vol. 2, 1871, pp. 254–255.

[c] Hubbard, L. L., Macroscopic minerals of Michigan: Rept. State Board Geol. Survey Michigan, 1891–92, p. 176.

and thus even the most soluble of the abundant elements have been fixed in the veins to some extent.

While the silicates are dominantly gangue minerals, silicates of zinc, manganese, and nickel occur as ores. Silicate of zinc occurs both as willemite ($2ZnO \cdot SiO_2$) and as calamine ($H_2O \cdot 2ZnO \cdot SiO_2$). The most notable occurrence of willemite is in the New Jersey zinc deposits.[a] In reference to this mineral the question arises whether it was formed as an original precipitate from the deep circulation or was produced by dehydration of calamine in the zone of anamorphism, the calamine having been formed originally in the belt of weathering in the same manner as in the Mississippi Valley. Whether calamine occurs as zinc ore as an original deposit by ascending waters I do not know. The abundant development of calamine in consequence of the reactions of the belt of weathering is very well known, as explained on pages 1144, 1147–1148.

Manganese silicate occurs rather abundantly as rhodonite ($MnO.SiO_2$). For the most part, however, this is a gangue mineral rather than an ore, its occurrence being well illustrated at Butte, Mont., and in the Smuggler Union mine and other places in the San Juan district, Colorado. Although sometimes found in considerable quantities, it is not now used in the United States as a source of manganese on account of its high percentage of silica.[b]

The most notable occurrence of nickel as a silicate is in New Caledonia. Packard says: "The nickel ore of New Caledonia is a hydrated silicate of nickel and magnesium (garnierite) which occurs intimately associated with serpentine. . . . The field observations showed that the nickel silicate is clearly an alteration product of the serpentine. . . . Hot springs have played a conspicuous part in furthering the decomposition of the nickel-bearing serpentine into garnierite and the other products."[c] Packard also notes the occurrence of nickel silicate at Riddles, Oreg., in North Carolina, in the Urals, and in Silesia. In all cases it is a secondary alteration product usually derived from a serpentine which itself was derived from a nickeliferous olivine. From Packard's descriptions it appears probable that the nickel silicate mined is an oxidized product formed by the reaction of

[a] Kemp, J. F., The ore deposits at Franklin Furnace and Ogdensburg, New Jersey: Trans. New York Acad. Sci., vol. 13, 1893–94, p. 90.

[b] Penrose, R. A. F., jr., Manganese, its uses, ores, and deposits: Ann. Rept. Geol. Survey Arkansas for 1890, vol. 1, 1891, p. 85.

[c] Packard, R. L., Genesis of nickel ores: Mineral Resources, 1893, pp. 170–171.

descending waters upon a sulphide of nickel, the latter being deposited by the deep circulation.

In conclusion, it appears that the silicates deposited by ascending waters, like the carbonates, are essentially gangue minerals. The only silicates deposited by ascending waters which may be ores are those of zinc, manganese, and nickel. It yet remains to be shown that any of these compounds are sufficiently abundant as first concentrates by ascending waters to serve as important ores.

CRITERIA FOR DISCRIMINATING DEPOSITS OF THE DEEP CIRCULATION.

The ascending waters depositing ores are necessarily those of the deep circulation. The criteria by which ores may be determined to have been deposited by ascending waters from a deep circulation have not yet been fully worked out, but certain suggestions may be made.

The first and most conclusive criterion discriminating ores produced by deep waters is that at the present time the waters are observed to be ascending. Locally, as in the Comstock lode, great volumes of hot water are rising, and doubtless ores are still being deposited. In such cases the evidence in favor of deposition from ascending waters is complete. A characteristic of ascending streams of the deep circulation is their independence of rainfall and other local conditions. The volume and the temperature of the water remains nearly constant from one year's end to the other. The best illustration of such an occurrence known to me is that furnished by the Comstock lode, already mentioned. An almost equally good case is that in the Smuggler Union mine at Telluride, Colo., where, about 600 meters below the surface, in the Pennsylvania shaft, a stream of water at a definite temperature rises with uniform flow entirely unaffected by the seasons. The regularity of the temperature and volume of this water have led to the use of the stream for mine purposes. Equally good instances of an extended rising circulation independent of local precipitation are found in the Joplin district of Missouri. Here in practically all of the sulphide mines below a very moderate depth there is unanimous agreement among the miners that the volume of water which rises is not influenced in the slightest degree by precipitation. Whether the season be dry or wet the steady flow of rising water must be handled. Where for some reason the process of concentration of the ores has ceased, as is doubtless the case in many regions, we do not find

evidence of the ascending waters. One of the common causes for the cessation of a vigorous underground circulation is the nearly complete cementation of the openings by the circulation. When the openings become subcapillary the circulation necessarily ceases.

Where there exist underground streams with steady flow the channels which they occupy are usually clean and fresh. They are lined with beautiful clear crystals without a stain. Along the channels there may be openings or even caves lined with crystals of various sizes, some of them reaching a foot or more in diameter. Such vugs, openings, and caves are superbly illustrated in the Joplin district of Missouri, where, in consequence of the lowering of the level of ground water by mining, such openings may be visited. When first freed from water the crystals lining the cavities are as untarnished as polished plate glass. The same thing may be seen at the Enterprise mine at Platteville, Wis., in the Upper Mississippi Valley. At this locality, as well as many in Missouri, the ores are clearly associated with the trunk channels of circulation. The miners in their operations follow the channels as guides, working against the streams. At places along a channel the water is concentrated into a single stream, and at such places there is likely to be comparatively narrow belts of very rich material along the walls. In other places the stream is subdivided among many small openings, and at such places the ore is dispersed.

Probably this criterion of ascending waters and freshness of the deposited material furnishes the best single line of evidence in favor of a deep circulation. But one must not conclude that the deposits of the ascending waters extend, unaffected by descending waters, to the very surface. For instance, while the present mining in the Joplin lead and zinc district of Missouri is in the belt in which descending waters have produced comparatively little effect, i. e., from 30 to 60 meters deep, at the surface and for a few meters below the surface descending and ascending waters mingled. Together they moved off laterally, and in consequence of their joint action the oxidized products and the galena deposits mentioned on pages 1444–1446 were produced. In this particular area the distance to which the descending water produced an effect is very small, but such is not universally the case. Where the vertical elements are greater and the relief is steeper, the descending waters working against the ascending currents may produce an effect to a very considerable depth.

The very marked difference between deposits made by deep waters and those made by shallow waters is beautifully illustrated by the Missouri district. Thus in Joplin, where pumping has lowered the level of ground water by 30 to 45 meters, the once clean openings, formerly below the ground-water level, are now in the belt where waters are descending. The caves which when first entered showed crystals fresh and untarnished are now coated with oxide of iron and other products carried by the descending waters. Still more striking is the contrast between the clean mines in which waters are ascending and the dirty ones in other areas in which descending waters have produced an important effect to a considerable depth. The latter mines are on smithsonite and calamine, and are muddy and dirty to the last degree. Thick, sticky, iron-stained clay is everywhere, adhering thickly to one's boots. The amazing contrast between the conditions of the two classes of deposits is illustrated by the sulphide mines of the Joplin camp and the oxidized product mines of the Aurora camp About 2 kilometers distant from Aurora is Sand Ridge, where the capping Carboniferous impervious shale still remains. Here the descending waters have not had a chance to enter, and the deep-seated waters are still rising, and in this mine, which is only a short distance from the dirty oxidized mines, are found the same clean sulphides and beautiful crystal-lined cavities so characteristic of the mines of Joplin.

In many cases, where currents are still rising, the ores are still being deposited. This is believed to be true in the lead and zinc district of southwestern Missouri, in the Comstock lode, and is known to be the case at Steamboat Springs and Sulphur Bank. Where, in mines, streams of clear water are found, with a uniform flow, unaffected by the seasons, and deficient in oxygen, the evidence seems conclusive that the ore deposits associated with such a circulation are the products of the deep circulation. But in many districts the conditions of circulation which resulted in the first concentration have ceased, the openings having been perhaps fully cemented at the time of concentration, thus causing the circulation to die out. In such cases the present circulation may be of an entirely different character, even if the first main concentration was that of deep waters.

A second criterion indicating that ores are deposited from the deep circulation is the phenomenon of crustification, so strongly emphasized by Posepny. (Fig. 28.) Posepny argues that the regular laminar arrangement

of different minerals or different combinations of minerals along the walls of a vein or along one wall is evidence that the waters have risen from a deep-seated source, the mineral solutions changing from time to time and so resulting in the banded or comb structure.[a] I follow Posepny in the belief that, in most cases, such regular crustification is especially characteristic of ores deposited by ascending waters. But undoubtedly, in many cases there are superimposed upon the primary crustification later similar minerals deposited by descending waters, as fully explained on subsequent pages. (See pp. 1146, 1151, 1152, 1154–1157.) Such secondary sulphides have been described at many localities, but so far as I know no one has claimed that such descending waters have added definite continuous secondary crusts, one above the other. Certainly it has never been shown that an ore deposit produced solely by descending waters shows a definite

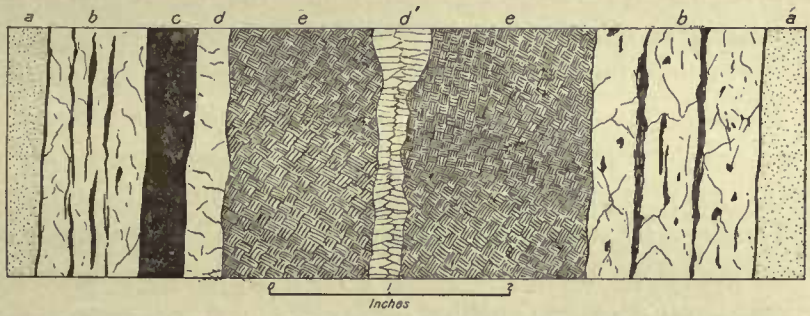


FIG. 28.—Cross section of banded vein near the London shaft, Mineral Point, Colo. *a*, country rock; *b*, quartz and chalcopyrite; *c*, tetrahedrite; *d d′*, quartz; *e*, galena. After Ransome.

crustification. It must be remembered that the existence of crustification is no evidence that the alternating minerals contained in the veins have not been modified and enriched by descending waters. Indeed, this is very frequently the case. Therefore crustification is an evidence of a first concentration by ascending waters, but is not evidence that descending waters have not since greatly modified the character of the deposit.

A third criterion which is of great importance in showing that ores are deposited from the deep circulation is the somewhat even tenor of values vertically. It is explained (pp. 1139–1143) that a special characteristic of descending waters is to produce a rich upper belt which diminishes in value with depth. It is shown, also, that one of the most characteristic effects of

[a] Posepny, F., The genesis of ore deposits: Trans. Am. Inst. Min. Eng., vol. 23, 1894, pp. 254–262.

descending waters is to produce a differentiation of the products, in a vertical sense, one mineral or one combination of minerals being at one horizon and another mineral or combination of minerals being at another horizon. Commonly these horizons have a depth varying from a few meters to many or even hundreds of meters. This is very different from the phenomena of crustification, in which the change of minerals is lateral within very short distances at right angles to the walls.

It is certain that for various reasons, as fully explained under "Ore-shoots," there are great variations vertically in the richness of deposits produced by deep waters. A case of such extreme variation is that of the Comstock lode of Nevada, where there were numerous great bonanzas separated from one another by comparatively lean material; and yet in this vein the evidence of water ascending under pressure is most conclusive, with no evidence of descending water; but the variations in tenor in deposits of the deep circulation are in both directions. The bonanzas may be found lower than the poorer material, and vice versa. In contrast with this, descending waters produce an upper rich belt which is not again duplicated below. While the deposits of the deep circulation may vary greatly in values, in many cases there is remarkably even tenor for great vertical depths. The best illustration of this known to me is the copper deposits of the Lake Superior region which are known to extend from the surface to a vertical depth of 1,600 meters, equivalent to 2,066 meters along the dip, 40°, with values sufficient to warrant working throughout the distance.

As already explained, the copper was in all probability reduced and precipitated directly as metallic copper from upward-moving cupriferous solutions. The reducing agents were ferrous solutions derived from the iron-bearing silicates, and ferrous compounds in the solid form, magnetite and silicate. It is well known that metallic copper once formed is but slowly affected by the oxidizing action. Oxidation has in fact occurred in the Lake Superior region, but not to an important extent. An oxidized belt may have formed in pre-Glacial time, but if so it was swept away by glacial erosion, and a sufficient interval has not elapsed to form another. The ore deposits now worked have apparently remained practically unchanged since their first concentration. In this fact we have the explanation of the extraordinary depths to which these deposits extend.

Lindgren cites the gold veins of Nevada City and Grass Valley, California, as another case of constant tenor. According to him,[a] "It can be confidently stated that there is no gradual diminution of the tenor of the ore in the pay shoots below the zone of surface decomposition," although within the same shoot there are many and great variations in richness. This statement is applicable to deposits which reach a vertical depth of 500 or 600 meters. If Lindgren is correct in thinking that the gold-quartz veins of the Sierra Nevada do not diminish in depth below an extremely superficial upper zone, this would be a case in which sulphuret ores were sufficiently concentrated by ascending waters alone to afford workable ore deposits.

In conclusion, it may be said that even tenors, in a vertical direction for any considerable depth, is very strong evidence of a concentration by ascending waters; but the reverse can not be said, that variability in a vertical direction is evidence that the deposits were not deposited by ascending waters.

Fourth. The absence of oxidized products in deposits, especially of limonite, favors the view that the ores were deposited by the deep circulation and were unaffected by secondary concentration; but this criterion is severely limited by the fact that enrichment of the sulphides takes place below the level of ground water in consequence of secondary descending solutions. An excess of base sulphides prevents the formation of the more palpable evidence of oxidizing waters.

Another difficulty in reference to using oxides as a criterion is that, in consequence of denudation, the ores deposited by the deep circulations rise into the belt of oxidation and are modified by the oxidizing waters to a variable extent. Very early in the process such oxidized products as hematite and limonite form. The ores are still essentially those of the deep circulation. From this stage to that in which the secondary action of oxidizing waters is of such consequence as to produce abundant hydrated hematite and limonite there are all gradations; but in many cases the secondary effect of descending, oxidizing waters can be allowed for and a judgment reached as to the nature of the deposit before it was modified by descending waters.

[a] Lindgren, Waldemar, The gold-quartz veins of Nevada City and Grass Valley, California: Seventeenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1896, p. 163.

In the case of a given ore deposit, by wise combination of the criteria given, it is in general possible to make a somewhat reliable judgment as to whether or not the ore was produced solely by ascending waters.

GENERAL STATEMENTS.

The foregoing statements explain to some extent the source, nature, and manner of deposition of the compounds deposited by ascending waters. But it is not the intention here to discuss their application to the known districts. This I do not attempt, because I lack the necessary accurate observations upon which such a discussion should be based. To tell in what manner the deposits of an individual district are formed requires very detailed investigation of that district.

While it is not the purpose here to take up the solution and deposition of the compounds which occur in individual ore deposits, it is well again to recall the law of mass action. Other things being equal, those compounds which are abundant will be dissolved in larger degree during the downward course of the waters, and will be most abundantly precipitated in the trunk channels. It is well known that, with the exception of aluminum, which does not form a sulphide, iron is the most plentiful of all the metallic compounds in the crust of the earth, and therefore iron sulphide occurs in greater abundance than the sulphide of any other metal. It is well known that in many cases the deeper a mine goes below the level of ground water the greater becomes the proportion of iron sulphide and the less that of the other metals. As a result of this, combined with increased cost of working, it frequently does not pay to mine a deposit beyond a certain depth. The law of mass action explains the abundance of the iron sulphide; it does not explain the frequent relative increase of the iron sulphide and the decrease of more valuable sulphides as one passes from the level of ground water into deeper workings. To explain this we must take into account the effect of the downward-moving waters, discussed under the succeeding heading.

We have now seen that the zone of fracture is traversed by the percolating waters; that metalliferous materials taken into solution by the downward and lateral moving waters are carried to the trunk channels of underground circulation, and that in these trunk channels the metalliferous materials are precipitated in various ways. Thus a first concentration by ascending waters, giving sulphurets, tellurides, and metals of some of the elements, is fully accounted for.

In some cases the deposits thus produced are rich enough to be of economic importance. In these cases, which undoubtedly exist, but which perhaps are less numerous than one might at first think, a first concentration by deep waters has been sufficient.

SUBCLASS 2. ORES PRECIPITATED FROM ASCENDING AND DESCENDING AQUEOUS SOLUTIONS.

Thus far ores precipitated by ascending waters alone have been considered. However, many of the ores thus produced have been profoundly modified by the action of descending waters.

Where the point of exit of the ascending waters of the trunk channels is in a valley or near the level of surface drainage the waters may reach the surface. However, where the openings are below slopes, ascending waters ordinarily do not continue to the surface, but make their way laterally from the trunk channels at and below the level of ground water. (See fig. 26.) Above the level of ground water, and frequently for a certain distance below it, the movement is downward in the openings. The water thus moving downward includes not only that which directly passes into the trunk openings at the surface, but a much larger quantity which converges into them from the smaller openings on all sides.

In regions in which mining is going on denudation has ordinarily truncated the veins for considerable depths, in many cases to hundreds or even thousands of meters. It is therefore clear that, in a majority of cases, the upper portions of the fissures in which the waters are now descending were in all probability much deeper below the surface, and therefore the waters in many of the larger fissures were once ascending. During the time the water was ascending the first concentration of sulphurets and other products took place. But as a result of the downward migration of the belt of weathering and the downward movement of water in that belt alteration and secondary concentration of ore deposits have taken place. This second concentration of ore deposits is of the greatest consequence, and I believe largely explains the frequent greater richness of the upper 50, or 100, or 500 meters, and in some cases 1,000 meters, as compared with lower levels.

As soon as denudation results in the transfer of the sulphides, tellurides, and metals of the first concentration into the belt of weathering they are subjected to the action of the descending waters bearing oxygen

and carbon dioxide. As denudation continues the belt of weathering continues to migrate downward. As a consequence of the reactions of the belt of weathering, combined with denudation, the character of the upper part of the lode is greatly changed, there being produced in the upper part of it a second concentration. If this process continues long enough under favorable conditions, the deposits formed may be divided into three belts: (1) Above the level of ground water, and in some instances extending somewhat below it, is a belt largely composed of oxides of manganese, iron, and copper; carbonates of lead, zinc, and copper; hydrated silicates of nickel and zinc; chloride of silver; metallic gold, silver, and copper; and residual enriched sulphides and tellurides; all with the associated gangue minerals. (2) At and below the level of ground water, and in some cases extending somewhat above it, is a transition belt composed of rich sulphides of silver, mercury, copper, lead, zinc, nickel, etc.; tellurides of gold and silver; and free gold, silver, and copper; with these are subordinate amounts of oxidized products and of course the associated gangue minerals. (3) Deeper down is a belt in which iron sulphides, pyrite, and pyrrhotite preponderate; but in which are considerable amounts of the more valuable sulphurets, the tellurides of gold and silver, and free gold, silver, and copper. Between the three classes of material there are gradations. The oxidized belt passes gradually into the rich sulphide and telluride belt; the rich sulphide and telluride belt passes gradually into the lean sulphide belt. It is not to be supposed that all of the above products are to be found in a single lode. The development of the belts is due to a complicated set of reactions caused by descending waters. These reactions will be more fully appreciated when individual combinations of metals are considered. Here only a brief general statement will be made.

In the belt of weathering the reactions which transform the original products—sulphides, tellurides, and metals—are oxidation, hydration, and carbonation, the fundamental reactions of the belt. In this belt the formation of the materials mentioned is but the result of the application of these general processes to the exceptional geological products, ore deposits. Before hydration and carbonation can take place oxidation must occur. If the sulphides be equally abundant, the sulphide which is most easily oxidized is the first to disappear. The order of disappearance for the metals in

this hypothetical case, as shown by the work of Anthon[a] and Schürmann,[b] omitting the less important elements, is therefore manganese, arsenic, iron, cobalt, nickel, zinc, lead, tin, antimony, copper, silver, mercury. It is, however, understood that the oxidation of an easily destroyed sulphide is not complete before the oxidation of a more refractory sulphide has begun. All of the sulphides are being oxidized all the time, but the more readily a sulphide is oxidized the more rapidly it is destroyed.

The sulphur of a sulphide may be oxidized without the oxidation of the metal, in which case a metal is produced by the process of oxidation. At the same time the sulphur is oxidized, or subsequently, the metal may also be oxidized, and thus oxides be formed. As soon as the oxides are produced they may unite with carbon dioxide and form carbonates, or with silicic acid and form silicates. If water also unites with the compounds the carbonates and silicates are hydrated. But the carbonates and silicates may also be produced in a different manner. The sulphides as originally oxidized may be tranformed to sulphates. If thus changed, the sulphates may immediately react upon carbonates or silicic acid, producing carbonates or silicates, at the same time forming sulphates of other elements, such as barium, strontium, or calcium. The evidence that reactions of this kind have taken place upon an extensive scale in veins is perfectly clear. In mine waters sulphates of copper, zinc, and iron occur very frequently. In some cases the amount of sulphate of copper in such water is so great that it is worth while to run it over iron and thus precipitate the copper. Further evidence of the formation of the sulphates is shown by the frequent precipitation of basic ferric sulphates in the veins, as, for instance, at Cripple Creek.[c] That the sulphates produced by oxidation of the sulphides react upon the other elements is shown by the frequent development in the upper part of the veins of such gangue minerals as barite, celestite, gypsum, and occasionally even magnesium sulphate.

An admirable case illustrating this principle is described by James Douglas. In speaking of the Arizona mines he says that gypsum is abun-

[a] Anthon, E. F., Ueber die Anwendung der auf nassem wege dargestellten Schwefelmetalle bei der chemischer Analyse: Jour. f. Prak. Chem., vol. 10, 1837, pp. 353–356.

[b] Schürmann, E., Ueber die Verwandtschaft der Schwermetalle zum Schwefel: Liebig's Ann. d. Chem., vol. 249, 1888, pp. 326–350.

[c] Penrose, R. A. F., jr., Mining geology of the Cripple Creek district: Sixteenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1895, p. 130.

dantly present in the driest mines of the Southwest, but at Bisbee, a more humid area, it is absent.[a] Probably the reaction producing the sulphate has taken place extensively in both areas, but in the driest area there was not sufficient amount of water to dissolve the calcium sulphate formed and hence it was precipitated as gypsum. The sulphates may even react upon the aluminum salts and form hydrous sulphate of aluminum. This occurs in the gold veins of California.[b]

The oxidized belt in some cases may be altogether above the level of ground water, but in other cases where the descending oxidizing solutions are strong may extend somewhat into the belt of cementation. An excellent case illustrating the almost perfect coincidence of the oxidized belt with the belt of weathering is furnished by the Monte Cristo district, described by Spurr. He says, "the zone between the surface of the ground and the lowest level of the ground-water surface is practically coincident with the zone of oxidation."[c]

It has been shown how the upper oxidized belt is produced, and next the manner of formation of the rich sulphide and telluride belt will be considered. The oxidized products, oxides, carbonates, and sulphates, may either in situ react upon the unaltered sulphides, or the carbonates, sulphates, and other oxidized compounds may be transported downward in solution and there react upon the sulphurets. In either case the result is to produce a richer sulphuret. The reactions may be between an oxide or a salt of a metal and its sulphide, for instance between the oxide or sulphate of copper and the sulphide of copper, as shown by the following equations:

$$6CuS+2Cu_2O=5Cu_2S+SO_2$$

and

$$6CuS+2Cu_2SO_4+3H_2O=5Cu_2S+2H_2SO_4+H_2SO_3$$

The reaction, however, may be between the oxide or salt of one metal and the sulphide of a second, as for instance, between zinc oxide, sulphate, or carbonate and iron sulphide. In this case a sulphide of the first metal is

[a] Douglas, James, The Copper Queen mine, Arizona: Trans. Am. Inst. Min. Eng., vol. 29, 1900, p. 535.

[b] Lindgren, Waldemar, The gold-quartz veins of Nevada City and Grass Valley, California: Seventeenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1896, p. 120.

[c] Spurr, J. E., The ore deposits of Monte Cristo, Washington: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, p. 859.

produced. Thus Stokes has shown that zinc carbonate and sodium carbonate together react upon iron sulphide as follows:

$$8FeS_2+14ZnCO_3+Na_2CO_3=14ZnS+4Fe_2O_3+Na_2S_2O_3+15CO_2$$

The particular reactions in an individual case depend upon the relative proportions and solubilities of the compounds present, upon the existing conditions of pressure and temperature, the amount of oxygen, etc. This will more clearly appear upon subsequent pages.

The deep belt in which the sulphides of iron are preponderant is that of the first concentration already considered on previous pages.

The concentrations by ascending and descending waters have been spoken of as if they were successive. In some instances this may be the case; but frequently it is much more probable that ascending and descending waters are at work upon the same fissure at the same time, and that their products are, to a certain extent, simultaneously deposited. For instance, under the conditions represented by fig. 26 there is taking place in the lower part of the fissure a first concentration by ascending waters and, in the upper part, a second concentration by descending waters. Between the two there is a belt in which both ascending and descending waters are at work. In an individual case the rich upper part of an ore deposit which is worked may now be in the place where ascending waters alone were first acting, where later, as a consequence of denudation, both ascending and descending waters were at work, and still later, where descending waters alone were at work. The more accurate statement for this class of ore deposits, therefore, is that deep or ascending waters are likely to be potent in an early stage of the process, that both ascending and descending waters may work together at an intermediate stage, and that descending waters are likely to be important in the closing stage.

The above general statement may perhaps be better understood if supplemented by a consideration of specific associations of the metals. The associations which are chosen for illustrative purposes are as follows: Associations (1) of lead, zinc, and iron; (2) of copper and iron; (3) of silver and gold with the base metals.

ASSOCIATION OF LEAD, ZINC, AND IRON COMPOUNDS.

In order to understand the relations of the lead, zinc, and iron compounds where they occur together in ore deposits, it seems advisable to consider an individual region rather than to make a general statement. An excellent illustration of the association of these metals is furnished by the deposits of the Mississippi Valley, and this region will therefore be considered.

FACTS OF OCCURRENCE.

In the Mississippi Valley, as is well known, in openings in limestones, lead and zinc minerals are associated with marcasite, pyrite, and some chalcopyrite.[a] Calcite and dolomite are abundant gangue minerals, as would be expected. Barite is also a common gangue mineral and locally is very plentiful. There are other gangue minerals which will not be taken into account. Since chalcopyrite is very subordinate, it will not again be alluded to.

The vertical order of occurrence in the region is commonly as follows: Above the level of ground water in the belt of weathering the dominant valuable minerals are galena and the oxidized ores—smithsonite, calamine, cerussite, and anglesite. Other oxidized ores occur in subordinate amount, but they will be ignored. The cerussite and anglesite frequently incrust the galena or are in crystals upon it. With the smithsonite and calamine there is some sphalerite. The smithsonite and calamine may extend 5 or 10 meters below the level of ground water, but deeper the oxidized products almost wholly disappear. The presence of oxidized products below the level of ground water is due in some cases to the occurrence of the material along a main channel of downward-percolating waters or to the well-known general downward movement of oxidizing water somewhat below the level of ground water; in other cases probably is due to a present higher level of ground water than in pre-Glacial time, as a result of depression and valley filling at the close of the Glacial epoch; and in still other cases is probably due to reactions between oxidized lead salts and sphalerite. (See p. 1150.) Below the galena and the oxidized ores are sphalerite and galena together, the former being dominant except in the Southeastern district of Missouri.[b]

[a] Chamberlin, T. C., The ore deposits of southwestern Wisconsin: Geol. of Wisconsin, vol. 4, 1882, pp. 380–393.

[b] Chamberlin emphasizes the inferior position of the zinc as compared with the lead and the association of the zinc and iron, but he does not consider the positions of these compounds with reference to the level of ground water. Loc. cit., pp. 488–491.

Associated with the sphalerite and galena are large amounts of marcasite and pyrite. For much of the region the workings have not extended far below the level of ground water, but in certain districts they have reached a considerable depth. In some places, as at Granby, Mo.,[a] deep exploration has shown pyrite and marcasite to dominate at the lowest level reached.

Under the present heading a full consideration of the concentration by ascending waters is excluded; but in order to consider the secondary work of descending waters it is necessary to outline the work of the first concentration by ascending waters.

In the Upper Mississippi Valley the order of occurrence of the minerals at many openings from the wall to the center of the veins or to the druses is marcasite, ferriferous sphalerite, galena in cubic crystals; or is sphalerite, galena. In some cases the order is marcasite, blende, these two being repeated perhaps several times. Not infrequently the galena of the first succession is followed by marcasite and (very subordinate in quantity) galena in octahedral crystals. Occasionally between the galena and the second marcasite is ferriferous sphalerite in small amount. If the druses are not fully closed by the sulphides there usually follows calcite, and occasionally barite on the calcite. Thus if there were a full succession at any one place, it would be (1) marcasite, (2) ferriferous sphalerite, (3) galena in cubic crystals, (4) ferriferous sphalerite, (5) marcasite, (6) galena in octahedral crystals, (7) calcite, (8) barite.

In the Lower Mississippi Valley sequences similar to those in the Upper Mississippi Valley occur in certain places, but in the best known and most productive district, that of southwestern Missouri, there seems to be no regular sequence for the sulphides. According to Bain, the general order of deposition for this district, within the openings, was dolomite, metallic sulphides, and chert. "To some extent these processes were contemporaneous or recurrent, but as a whole they occur successively in the order named." As to the relations of the sulphides to one another, Bain says: "Blende rests on galena and galena on blende indiscriminately, and both cover and in turn are covered by iron sulphide."[b] Also blende and galena are in many cases intimately intermingled.

[a] Bain, H. F., with Van Hise, C. R., and Adams, G. I., Preliminary report on the lead and zinc deposits of the Ozark region: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, p. 162.

[b] Bain, H. F., cit., pp. 151–152.

I know of no clearer illustration of the phenomenon of crustification described by Posepny, and indeed of the general principles of ore deposition by underground waters, than that furnished by the Upper Mississippi Valley district. The larger parts of the crustified sulphide products are believed to be the work of ascending waters. In many cases it appears that there were two or more cycles of precipitation, so far at least as the sphalerite and galena are concerned, but the first cycle was by far the more important. As explained below, it is thought to be probable that the galena in octahedral crystals (No. 6 of the general succession), and in many cases the sphalerite (No. 4) and the marcasite (No. 5), are due to a second concentration.

As to the manner of transportation of the metals which in the Mississippi Valley were precipitated as sulphides at the first concentration, it is believed that the lead and zinc travelled mainly as oxidized salts, and probably largely as sulphates. All the evidence goes to show that in this region the concentration took place under physical conditions substantially the same as those which exist at the present time. There is no proof that the solutions went to any great depth, or that unusual temperatures prevailed. Nor is there any evidence that abundant alkaline sulphides and carbonates of the alkalies were present. Therefore, it can not be supposed that the sulphides were transported as such. Probably they were originally disseminated through the limestones as sulphides, were oxidized to sulphates and transported in that form, or as carbonates.

The first precipitation of the ascending salts is believed to have been accomplished through the agency, direct or indirect, of organic matter. There is abundant organic material in the shales associated with the ores, and a less amount in the limestones. While the precipitation of the sulphides disseminated through the shales may have been largely accomplished by the direct reaction of the solid carbonaceous material, the more common precipitation within the openings was probably accomplished through the reducing solutions which were produced by the contact of the water with the organic compounds. Waters which have been in contact with such compounds, which also bear sulphides, are very likely to contain hydrogen sulphide. This substance is a direct precipitant of the sulphates as sulphides, but it is probable that dissolved organic compounds also act as reducing agents at the point of precipitation in the crevices.

SECOND CONCENTRATION.

It is highly probable that the regular vertical distribution of the minerals is due to a second concentration mainly controlled by downward-moving waters combined with denudation.

OXIDIZED ORES.

The oxidized ores include those above or near the ground-water level. As already noted, the important ones comprise smithsonite, calamine, cerussite, and anglesite. These ore bodies have been formed from the sulphides by oxidation, carbonation, and hydration. The beginning of these processes is coincident with the appearance of the sulphides above the level of ground water in consequence of progressive denudation. Lead sulphide (PbS) and zinc sulphide (ZnS), by simple oxidation are changed to lead sulphate ($PbSO_4$) and zinc sulphate ($ZnSO_4$). The lead sulphate constitutes the mineral anglesite. If this sulphate in solution reacts upon calcium carbonate, lead carbonate and hydrated calcium sulphate are produced according to the following equation:

$$PbSO_4+CaCO_3+2H_2O=PbCO_3+CaSO_4.2H_2O.$$

If zinc sulphate reacts on calcium carbonate, smithsonite is produced according to the following equation:

$$ZnSO_4+CaCO_3+2H_2O=ZnCO_3+CaSO_4.2H_2O.$$

In this connection it is interesting to note that in Wisconsin the smithsonite often occurs in beautiful pseudomorphs after the various forms of calcite characteristic of the district. In many cases when these pseudomorphs are broken they are found to be partly hollow, showing not only that the calcite was replaced, but that solution of the calcium carbonate went on faster than the deposition of the smithsonite. In many other instances the smithsonite is in plates of greater or less thickness over calcite or limestone, the latter showing solution by unequal etching.

Where the zinc sulphate finds abundant amorphous silica in chert the reaction may be between this compound and the zinc salt in the presence of water, the equation being as follows:

$$SiO_2+2ZnSO_4+3H_2O=(ZnOH)_2SiO_3+2H_2SO_4.$$

In the Upper Mississippi Valley chert is not abundant and in that district the chief oxidized zinc ore is smithsonite. In the southwestern district of Missouri chert is very abundant, and the dominant oxidized ore is calamine, although smithsonite is also there present in important amounts.

The oxidized ores are often very rich and frequently they are concentrated in large irregular masses. These features, exceptional as compared with the sulphides of the first concentration, are due to two processes: First, through downward transportation by the solutions there may be segregated in a small vertical distance a large part of the materials which had a wider vertical distribution as sulphides; and second, residual concentration takes place—that is, the carbonates and sulphates of lead and zinc are much more insoluble and heavier than the country rock with which they are associatated—the limestone. As the limestone is eroded the oxidized deposits sink down and thus accumulate.

SULPHIDE ORES.

Galena.—If it be premised that the ascending waters evenly distributed the sulphides, at least so far as the vertical element is concerned, although across the vein these sulphides may or may not be arranged in a definite order, it is certain that downward-moving waters, combined with denudation, may concentrate the galena at high levels and the sphalerite at lower levels. (See pp. 1144–1145.)

Galena is the most difficultly oxidizible of the sulphides of lead, zinc, and iron. (See p. 1140–1141.) Moreover, this compound is immeasureably more insoluble than the limestone. By the solution and mechanical erosion of the limestone and by the oxidation and solution of the sphalerite and iron sulphide above the level of ground water, the galena is concentrated. Whitney estimates that to make one-third meter of residual clay in the lead and zinc district of Wisconsin requires 10 to 12 meters of limestone and shale.[a] Since in this district the residual material is often several meters thick, it follows that at and near the surface there may be concentrated as a residual product an amount of galena which was originally distributed through several or many meters of limestone. That these processes of erosion of the limestone and the removal of the sphalerite and marcasite by oxidation have taken place upon an extensive scale is shown by the

[a] Hall, James, and Whitney, J. D., Geology of Wisconsin; vol. 1, 1862, pp. 121–125.

occurrence of many detached fallen crystals and masses of galena in the openings above the level of ground water, and also at the bottoms of the wider openings and caves a short distance below it. Indeed, a considerable portion of the lead which has been mined was taken above or within a short distance below the level of ground water. This strongly corroborates the idea that concentration resulted from the solution of the other sulphides which held the galena to the walls and from the erosion of the limestone, thus permitting the material to drop to lower positions in the crevices.

While the concentration of the galena was partly as above stated, it may have been caused in part by chemical reactions between the various compounds. In the belt of weathering part of the galena, as already noted, is being oxidized, as is shown by the incrustations and superimposed crystals of cerussite and anglesite. During the formation of the carbonates and sulphates a certain amount of these salts is taken into solution and carried downward. These carbonates and sulphates react upon the other sulphides present and reprecipitate the lead as galena. These reactions may take place to some extent above the level of ground water, but are especially likely to occur below it. As a result of the downward migration of the belt of weathering, there is in the downward-moving waters a continual supply of the sulphates and carbonates of lead. The chief reaction is that between the lead salts and the dominant iron sulphide. Supposing the iron were in the form of FeS, the reactions may be written as follows:

$$PbSO_4+FeS=PbS+FeSO_4.$$
$$PbCO_3+FeS=PbS+FeCO_3.$$

If the iron be supposed to be in the form of FeS_2, as is most likely, and oxygen were present, the reactions may be—

$$PbSO_4+FeS_2+O_2=PbS+FeSO_4+SO_2.$$
$$PbCO_3+FeS_2+O_2=PbS+FeCO_3+SO_2.$$

Stokes has also shown that the precipitation of lead as a sulphide from its oxidized solutions may be accomplished by the bisulphide of iron without the presence of oxygen. The reaction by which this takes place is as follows, with lead sulphate:

$$7PbSO_4+4FeS_2+4H_2O=7PbS+4FeSO_4+4H_2SO_4.$$

A similar reaction takes place with lead carbonate and bisulphide of iron where sodium carbonate is present. Stokes writes the reaction as follows:

$$14PbCO_3+8FeS_2+Na_2CO_3=14PbS+4Fe_2O_3+Na_2S_2O_3+15CO_2.$$

Subsequent experiment has shown that calcium carbonate may be substituted for the sodium carbonate. The last two reactions were performed at temperatures of 100° and in the absence of oxygen. Since in the upper part of ore deposits such temperatures are seldom found, and there is no reason whatever to suppose that they existed during the development of the lead and zinc ores of the Mississippi Valley, and as oxygen is likely to be present, it is probable that the precipitation of the sulphide of lead by the bisulphide of iron in the upper part of veins was by the reactions written with oxygen rather than by the reactions without oxygen.

However, it has been stated that zinc sulphide is present with the original sulphides, and this may also react upon the lead salts, according to the following equations:

$$PbCO_3+ZnS=PbS+ZnCO_3.$$
$$PbSO_4+ZnS=PbS+ZnSO_4.$$

In the case of the former reaction, smithsonite would be formed. In this connection it is notable that frequently smithsonite is associated with the galena for some distance below the level of ground water. While a part of the smithsonite below ground water is of this origin, doubtless the larger portion of it is differently explained. (See p. 1147.)

To the foregoing reactions, partly explaining the concentration of galena, objection may be made on account of the slight solubility of lead carbonate and lead sulphate. It is true that these substances are very sparingly soluble in pure water; however, they are sufficiently soluble in waters bearing carbon dioxide to account for the phenomenon. But some of the lead may have been carried downward as a chloride. Independently of chemical theory, we know that much of the galena has been changed to some soluble form upon an extensive scale. As evidence for this inference, galena crystals above the level of ground water are much corroded, and the amount of cerussite and anglesite associated with them is so small as not to account for the corrosion, therefore the lead has been transformed to a soluble salt which has been transported below in important amounts. In the deposits of southwestern Missouri, and in those of Wisconsin adjacent to

the oil rock, which have by denudation passed into the belt of weathering, numerous partially dissolved crystals of galena in openings and many cubical openings once evidently occupied by galena but now wholly vacant show abundant evidence of oxidation and solution of lead sulphide.

Whether or not the reactions written above express the exact chemical changes, it is certain that oxidized lead salts are precipitated by the sulphide of iron and by the sulphide of zinc as lead sulphide, as was shown by the experimental work of Anthon and Schürman already referred to. (See pp. 1114–1115.)

So far as my argument is concerned, it is of no consequence whether the lead be transported as a sulphate, carbonate, chloride, or other salt. However, it is believed that these are the forms in which the lead was transferred on the most extensive scale. I regard the cerussite and anglesite as evidence of the partial transfer of the lead as sulphate and carbonate. A large amount of sulphate and carbonate probably formed, but the compounds are so insoluble that a part of the salts produced was not carried downward, but precipitated near the places of formation.

In the upper Mississippi Valley for a short distance above and below the level of ground water there are cubic crystals of galena of very large size as compared with those disseminated through the sphalerite at lower levels. The crystals at this upper horizon are commonly from 5 to 8 centimeters in diameter, and a considerable proportion have diameters of 10 centimeters and some of 15 to 20 centimeters. In contrast with this, the galena intimately associated with the sphalerite at the lower levels is very rarely in crystals larger than 5 centimeters in diameter, while a large part of it is in smaller particles. It is thought probable that the large size of the crystals at the upper horizons is the result of additions made by descending water to the smaller crystals of the first concentration Below the level of ground water octahedral crystals of galena are frequently superimposed upon the cubic crystals of this compound.

Sphalerite.—Evidence of the oxidation of sphalerite and the transportation of the material elsewhere is as clear as in the case of galena, both in the upper and lower Mississippi Valley. At many places in southwestern Missouri sphalerite crystals may be seen in the chert in various stages of oxidation, and the porous rocks contain numerous casts of the sphalerite crystals, now vacant or occupied by a film of iron oxide. Precisely the

same thing may be seen in Wisconsin, only that the matrix holding the partly dissolved sphalerite crystals or casts is limestone instead of chert.

The sphalerite oxidized to sulphate is carried downward. Zinc holds sulphur less strongly than lead, but much more strongly than iron. Therefore, the sulphate is reduced to sulphide below the galena, the reactions being similar to those producing the galena. They may be written as follows:

$$ZnSO_4+FeS=ZnS+FeSO_4,$$
$$ZnCO_3+FeS=ZnS+FeCO_3,$$

or,

$$ZnSO_4+FeS_2+O_2=ZnS+FeSO_4+SO_2,$$
$$ZnCO_3+FeS_2+O_2=ZnS+FeCO_3+SO_2.$$

While these, and especially the last two, are regarded as probable reactions, Stokes has shown that at temperatures from 100° to 180° C. precipitation may take place without the presence of oxygen, thus:

$$14\ ZnCO_3+8\ FeS_2+Na_2CO_3=14\ ZnS+4\ Fe_2O_3+Na_2S_2O_3+15\ CO_2$$

Under the conditions accompanying this reaction, calcium carbonate may be substituted for sodium carbonate, but the reaction is slower. While it has not been shown by experiment, it is probable that, in analogy with the reaction of copper sulphate and lead sulphate, zinc sulphate may at these higher temperatures react upon FeS_2 as follows:

$$7\ ZnSO_4+4\ FeS_2+4\ H_2O=7\ ZnS+4\ FeSO_4+4\ H_2SO_4$$

As confirmatory of the deposition of secondary sphalerite by the reactions above written or by other reactions which produce the same result, Bain has found in the Joplin district[a] of Missouri at various places ruby-colored crystals of sphalerite superimposed upon the main mass of sphalerite attributed to the first concentration.

Marcasite and pyrite.—At a certain depth in the openings below the level of ground water nearly all of the salts of lead and zinc descending from the belt of weathering would be precipitated by reactions between them and the iron sulphide, as above explained. In veins in which the first concentration extends to a depth greater than that to which downward-moving waters are effective, only the sulphurets of the first concentration would be

[a] Bain, H. F., Van Hise, C. R., and Adams, Geo. I., Preliminary report on the lead and zinc deposits of the Ozark region: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, p. 161.

found below this level. These sulphurets might consist mainly of marcasite and pyrite, with subordinate amounts of sphalerite and galena. However, even in this deep belt, concentration of galena and sphalerite may occur to some extent, although it receives no contribution from the lead and zinc salts from above; for even after the salts of lead and zinc traveling downward from the belt of weathering are all precipitated, the waters may still hold oxygen. This oxygen would, to the largest extent, act on the marcasite, producing to some extent soluble salts which would be abstracted, and thus reduce the quantity of this material, and relatively enrich the deposits in lead and zinc, although not increasing the absolute amount of lead and zinc present in a given vertical distance. So far as the zinc and lead salts were oxidized by the oxygen-bearing water, these would react on the iron sulphide again, and they would be precipitated according to the reactions given above.

The above paragraph can not be said to apply generally to the deposits of the Mississippi Valley. These deposits are usually of very limited vertical extent. Many of them are apparently cut off by impervious strata within short distances of the surface, but drilling at the Granby area, Missouri, has developed a large amount of pyrite at depth, and thus, so far as information goes, this area appears to conform to the general rule. In the upper Mississippi Valley area, while information is not very full, apparently below the galena horizon the iron sulphide is rather more abundant at high than at low horizons. As a consequence the zinc sulphides become less impure with depth. This has been noted at Shullsburg, at Platteville, at Benton, at Dubuque, and at Mineral Point. But this is in the belt in which marcasite and sphalerite alternate in the crustified ores, and both are apparently for the most part the products of ascending water. If this vertical distribution be regarded as chiefly due to the primary concentration by ascending water, the order is as it should be, for at first the zinc sulphide should be thrown down to a greater extent than the iron sulphide.

GENERAL STATEMENTS.

It is believed that concentration by ascending waters largely explains the crustified sulphide deposits of zinc and lead of the upper Mississippi Valley, at least so far as their main masses are concerned, although, as has been explained, superimposed upon the sulphides of the first concentration

are subordinate amounts of sulphides of the second concentration. It is believed also that the intimately intermingled sulphides at the lower horizons in southwestern Missouri and the great disseminated deposits in the massive limestone of southeastern Missouri are results of the first concentration. It is thought that a second concentration by descending waters explains through the reactions given the orderly distribution of the ores in a vertical direction, i. e., the oxidized products and the enriched galena above and near the ground water and the sphalerite deposits below the level of ground water. The intermingled sphalerite and galena below the level of ground water, while largely of the first concentration, are modified to a variable extent by the second concentration. Further, it is believed that the second concentration was a determinative factor in the production of many of the rich deposits, especially their upper portions. The process of concentration by descending waters is primarily chemical, but is also to some extent mechanical. The latter is especially true of the galena loosened by solution from the walls and of the oxidized products mixed with galena which have accumulated as residual material in consequence of erosion of the limestone.

The above conclusions were reached from a study of the facts in the field, without any knowledge of the experimental work in the laboratory showing that iron sulphide precipitates zinc and lead as sulphides from their oxidized salts, and that zinc sulphide precipitates lead as a sulphide from its oxidized salts. It is thus seen that the facts in the field and the experimental work of the laboratory supplement each other and strongly confirm the correctness of the conclusions as to the manner in which the vertical distribution of the ores is explained.

Thus the above theory fully explains and harmonizes the following:

(1) The galena and sphalerite crystals are frequently corroded and partly dissolved, and very numerous casts of them are found in the chert and limestone. These facts show conclusively that the sulphides have been dissolved above the level of ground water.

(2) Upon the calcite, and frequently pseudomorphous after its crystals, smithsonite is found, the calcite at these places showing corrosion and solution. This furnishes strong evidence that the oxidized salt of zinc, probably zinc sulphate, has reacted upon the calcite.

PLATE XII.

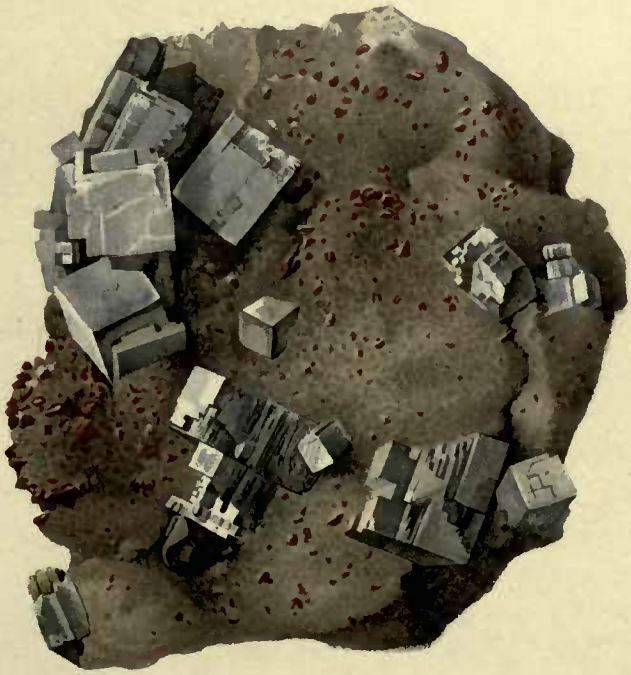
1155

PLATE XII.

A. Vein quartz, Banner mine, California. Showing shattering of black argillite by quartz seams; pyrite developing in the argillite but not in the quartz; further, brownish (weathered) carbonate deposited next to the argillite in the seams. Beginning of metasomatic alteration apparent by bleaching of the black argillite. After Lindgren.

B. Secondary galena and blende in ores from Missouri. After Bain.

(A)



(B)

JULIUS BIEN & CO. LITH. N.Y.

(A) VEIN QUARTZ, BANNER MINE, CALIFORNIA.
(B) SECONDARY GALENA AND BLENDE IN ORES FROM MISSOURI.

(3) With the oxidized products of lead and zinc are associated barite and gypsum. These are the by-products which should be formed by the reactions of the sulphates of lead and zinc upon the alkaline earth carbonates.

(4) At and near the level of ground water are very large crystals of galena as compared with those deeper in the deposits. These crystals are fully explained by secondary growths of galena deposited by descending waters.

(5) The products have a vertical order; the oxides, carbonates, and silicates lie mainly above the level of ground water, the galena largely above but extending below it, and the sulphide of zinc with the iron sulphides mainly below it. This vertical order is that which should be produced by the reactions of the descending oxidized salts of lead and zinc on the sulphides of zinc and iron.

(6) Superimposed upon the crustified sulphides of the first concentration are later crystals of galena and sphalerite, often different in character from the earlier sulphides. For instance, in Wisconsin the later galena is usually in octahedral crystals, and in Missouri the sphalerite is pure and ruby colored. (See Pl. XII, *B*.) The exceptional appearances of these products are fully explained by the reactions between the oxidized products of lead and zinc and the sulphides deposited by the first concentration.

While the precipitation at the second concentration of downward-moving sulphates is partly accomplished, as has been explained, by the reaction upon them of the low-grade sulphurets, thus producing rich sulphides, the reduction and precipitation of these oxidized products is partly accomplished by the direct and indirect action of the organic matter, precisely as in the case of the original precipitation. The power which organic matter has for the reduction and precipitation of the oxidized products has been recognized by several others who have written upon the lead and zinc of the Mississippi Valley. Among these are Chamberlin,[a] Blake,[b] Bain,[c] and Grant.[d]

[a] Chamberlin, T. C., The ore deposits of southwestern Wisconsin: Geol. of Wisconsin, vol. 4, 1882, pp. 544, 546.

[b] Blake, Wm. P., Lead and zinc deposits of the Mississippi Valley: Trans. Am. Inst. Min. Eng., vol. 22, 1894, pp. 630–631. Also, Wisconsin lead and zinc deposits: Bull. Geol. Soc. America, vol. 5, 1894, pp. 28–29.

[c] Bain, H. F., with C. R. Van Hise and G. I. Adams, Preliminary report on the lead and zinc deposits of the Ozark region: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, p. 213.

[d] Grant, U. S., Preliminary report on the lead and zinc deposits of southwestern Wisconsin: Bull. Wis. Geol. and Nat. Hist. Survey, No. 9, 1903, p. 83.

Chamberlin states that organic matter from the surface may have made its way down through the openings of the limestone, and thus assisted in the reduction of the descending oxidized products.[a] As pointed out by Blake, the effect of the organic matter is especially clear in the case of the large sphalerite deposits of Wisconsin which rest upon the oil rock at the base of the Galena.

While the above statement concerning concentrations of the lead and zinc ores by ascending and descending waters combined is made with reference to the Mississippi Valley, it is believed that many of the lead and zinc districts of other parts of the world have had a substantially similar history.

ASSOCIATION OF COPPER AND IRON COMPOUNDS.

Another very general association of metals is that of copper and iron. Where this association occurs it is well known that above the level of ground water metallic copper, cuprite (Cu_2O), tenorite (CuO), malachite ($CuCO_3.Cu(OH)_2$), and azurite ($2CuCO_3.Cu(OH)_2$) are very frequently found.

These compounds may be produced from any of the sulphides. It is not worth while to attempt to write out the reactions showing their formation from all of the sulphides, but to make the principles clearer it may be well to consider one illustrative case. For this purpose chalcocite is taken, since this is the richest sulphide and the one which, as shown below, is likely to be developed in the upper part of the belt of cementation and pass in large quantity into the belt of weathering. By simple oxidation of the sulphur of chalcocite, metallic copper is produced, according to the following reaction:

$$Cu_2S+2O=2Cu+SO_2$$

Simultaneously, or later, the metallic copper thus formed may be oxidized to cuprite, according to the equation:

$$2Cu+O=Cu_2O$$

By further oxidation the cuprite may pass into tenorite, according to the reaction:

$$Cu_2O+O=2CuO$$

[a] Chamberlin, cit., pp. 544–545.

When the oxidation has gone far enough to produce tenorite, carbonation and hydration may take place, and malachite be produced, according to the following reaction:

$$2CuO+CO_2+H_2O=CuCO_3 . Cu(OH)_2$$

Or if the carbonation goes further as compared with hydration, azurite may be produced, according to the following reaction:

$$6CuO+4CO_2+2H_2O=2[2CuCO_3 . Cu(OH)_2]$$

The product represented by any stage in this process may be regarded as formed directly by a combination of two or more of the preceding reactions. But in the southwestern portion of the United States it is certain that the reactions frequently if not usually occur step by step, as is shown by numerous specimens In a single specimen I have seen a core of chalcocite surrounded by metallic copper, outside of which is cuprite; beyond this lies tenorite, and beyond the tenorite hydrated carbonate. While it is rather rare to find this full succession, it is easy to get specimens of metallic copper interlaced or surrounded by cuprite, the latter being surrounded by at least a film of tenorite, beyond which occur the carbonates. In this connection it may be recalled that cuprite is a rather abundant oxide and that tenorite is rare. The reason which may be suggested for this is that as soon as tenorite is formed this oxide may unite with carbon dioxide and water and produce malachite or azurite. This process goes on almost as fast as the tenorite develops, and thus very little of this oxide is found in the mines. The oxidized copper products, instead of being formed from chalcocite, may be produced from any of the leaner sulphides of copper; but in such cases the associated iron forms iron compounds which may largely remain in situ as oxides or be carried away as sulphates.

The oxidized ores of copper occur extensively in arid regions. The precipitation is small, but there is enough moisture underground to carry on the work with the assistance of oxygen and carbon dioxide. In such a region the level of ground water is far below the surface and erosion is exceedingly slow, so that there is ample room and sufficient time for a large amount of material to accumulate above the level of ground water. In humid regions, while water is more abundant and the conditions to that

extent are more favorable to the development of the oxidized products, denudation is frequently so rapid that time is not given for the transformation of the sulphides to such products, for a given part of the belt of weathering is above the level of ground water only a short time before the material of that portion is removed by erosion. Also the belt above the level of ground water is narrow, and thus there is comparatively little room for the oxidized deposits.

While under favorable conditions oxidized products are very common above the level of ground water, it is well known that below it the oxidized and carbonated products occur in greatly diminished quantity, and there are frequently present rich sulphurets, such as chalcocite (Cu_2S), bornite (Cu_3FeS_3), chalcopyrite ($CuFeS_2$), and sometimes covellite (CuS). Somewhat deeper below the level of ground water the oxides and carbonates are not found. Furthermore, the chalcocite, covellite, and bornite are very generally restricted to the upper part of the belt of cementation; deeper, the places of these minerals are largely occupied by chalcopyrite. Not only is this true, but still deeper in many instances the chalcopyrite is less prominent, and the iron sulphides more so. In the lower workings of many of the deeper mines the only metalliferous product found is cupriferous iron sulphide, the chalcopyrite having wholly disappeared. But in some places where the dominant sulphide of the deeper levels is pyrite or pyrrhotite fracture openings within these sulphides are filled with the rich copper sulphides.

Whether or not this general statement is correct for a particular area, each mining engineer can judge from his own knowledge. There may be exceptions to it, due to various causes, one of which has been alluded to in explaining bonanzas. Thus below cupriferous pyrites there may again be found richer copper sulphides. Indeed, as before stated, ore deposits vary greatly in their richness both horizontally and vertically, and the above statement can only be considered as a general average.[a]

The above order is believed to be explained by the work of downward-moving waters. The combinations of lead, zinc, and iron were followed from above downward. The reactions which occur in the case of the copper-iron deposits may perhaps be followed, to vary the treatment, from the base

[a] See Raymond, R. W., Discussion of "Genesis of ore deposits," by F. Posepny: Trans. Am. Inst. Min. Eng., vol. 24, 1895, pp. 991–992.

upward. At greater or less depths below the level of ground water the ores are often dominantly cupriferous pyrites or pyrrhotite, the direct deposit of the ascending waters. At a little higher level oxygen from above may have oxidized a portion of the iron and transported it elsewhere, relatively enriching the deposit in copper; at a still higher level there is a contribution of soluble copper salts from above. Since copper sulphate is certainly the most common salt, for convenience all the soluble salts will be regarded as sulphates. Reactions similar to those given below may easily be written for other salts.

At the level where salts of copper appear from above, the action of the copper salt on iron sulphide may produce chalcopyrite, the reactions resulting from the greater affinity of sulphur for copper as compared with iron, and from the law of mass action. With cupric sulphate the reaction may be written, for ferrous sulphide:

(1) $2FeS+CuSO_4=CuFeS_2+FeSO_4$

For bisulphide of iron, in the presence of oxygen, the reaction may be:

(2) $2FeS_2+CuSO_4+O_4=CuFeS_2+FeSO_4+2SO_2$

or, if oxygen be absent,

(3) $7CuSO_4+8FeS_2+8H_2O=7CuFeS_2+FeSO_4+8H_2SO_4$

Where the iron sulphide is pyrrhotite, intermediate between FeS and FeS_2, the reactions may be written by combining the equations (1) and (3) in proper proportions.

The chalcopyrite may also be produced by the reaction of cuprous sulphate on pyrite or marcasite. In the presence of oxygen the reaction is as follows:

$3FeS_2+Cu_2SO_4+4O=2CuFeS_2+FeSO_4+2SO_2$

and in the absence of oxygen:

$15FeS_2+7Cu_2SO_4+8H_2O=14CuFeS_2+FeSO_4+8H_2SO_4$

In passing upward from the lowest level at which the chalcopyrite appears, this mineral may steadily increase in quantity until it becomes an important constituent, and finally the iron sulphide may become subordinate. Under these circumstances bornite is likely to appear also. The produc-

tion of bornite by the direct reactions of the cupric salts may be supposed to be as follows:

For ferrous sulphide in the presence of oxygen the reaction is:

(1) $4FeS+3CuSO_4+2O=Cu_3FeS_3+3FeSO_4+SO_2$

For iron bisulphide the reaction is:

(2) $3FeS_2+3CuSO_4+4O=Cu_3FeS_3+2FeSO_4+4SO_2$

or, if oxygen be supposed to be absent, the reaction for cupric salt may be:

(3) $13FeS_2+21CuSO_4+20H_2O=7Cu_3FeS_3+6FeSO_4+20H_2SO_4$

The production of bornite by the direct reaction of cuprous sulphate on the bisulphide of iron in the presence of oxygen may be written:

(4) $5FeS_2+3Cu_2SO_4+8O=2Cu_3FeS_3+3FeSO_4+4SO_2$

or, if no oxygen be present, the reaction is:

(5) $23FeS_2+21Cu_2SO_4+16H_2O=14Cu_3FeS_3+9FeSO_4+16H_2SO_4$

However, the bornite may also be produced by the reaction of the cupric salt on the chalcopyrite itself. For instance, in the presence of oxygen, for cupric sulphate, the reaction might be:

(6) $2CuFeS_2+CuSO_4+2O=Cu_3FeS_3+FeSO_4+SO_2$

If oxygen be absent the reaction for cupric sulphate would be:

(7) $13CuFeS_2+11CuSO_4+8H_2O=8Cu_3FeS_3+5FeSO_4+8H_2SO_4$

The reaction for cuprous sulphate in the presence of oxygen may be written:

(8) $4CuFeS_2+Cu_2SO_4+6O=2Cu_3FeS_3+2FeSO_4+SO_2$

and in the presence of oxygen:

(9) $23CuFeS_2+11Cu_2SO_4+4H_2O=15Cu_3FeS_3+8FeSO_4+4H_2SO_4$

Further reacuions might be written by combining corresponding equations for cupric and cuprous salts, as a result of which the bornite is produced by the reaction of both cuprous and cupric compounds. Reactions might also be written by which the bornite is partly produced from bisulphide of iron and partly from chalcopyrite. These reactions would be merely the combination of corresponding equations, and it seems hardly necessary to write them out, since no new principle is illustrated.

Still higher up, chalcocite may appear with the chalcopyrite and bornite. For a short distance below the level of ground water this mineral in some mines is the dominant sulphide and may be produced by the reaction of cupric sulphate on the iron sulphide. For ferrous sulphide the reaction in the presence of oxygen would be:

(1) $2FeS+2CuSO_4+2O=Cu_2S+2FeSO_4+SO_2$

For iron bisulphide in the presence of oxygen, the reaction would be:

(2) $2FeS_2+2CuSO_4+6O=Cu_2S+2FeSO_4+3SO_2$

or, if oxygen be absent, the reaction is:

(3) $5FeS_2+14CuSO_4+12H_2O=7Cu_2S+5FeSO_4+12H_2SO_4$

Chalcocite may be produced also by the reaction of cuprous salts on iron sulphide. For ferrous sulphide in the presence of oxygen the reaction is:

(4) $FeS+Cu_2SO_4=Cu_2S+FeSO_4$

for iron bisulphide in presence of oxygen:

(5) $FeS_2+Cu_2SO_4+2O=Cu_2S+FeSO_4+SO_2$

or, if oxygen be absent,

(6) $4FeS_2+7Cu_2SO_4+4H_2O=7Cu_2S+4FeSO_4+4H_2SO_4$

Furthermore, the chalcocite may be produced by reactions of the sulphates either on the chalcopyrite or on the bornite. In the case of cupric sulphate upon chalcopyrite in the presence of oxygen, the reaction may be written as follows:

(7) $CuFeS_2+CuSO_4+2O=Cu_2S+FeSO_4+SO_2$

or, if oxygen be not present, the reaction may be as follows:

(8) $5CuFeS_2+11CuSO_4+8H_2O=8Cu_2S+5FeSO_4+8H_2SO_4$

For cuprous sulphate upon chalcopyrite, in the presence of oxygen, the reaction is:

(9) $2CuFeS_2+Cu_2SO_4+6O=2Cu_2S+2FeSO_4+SO_2$

and in the absence of oxygen is:

(10) $8CuFeS_2+11Cu_2SO_4+4H_2O=15Cu_2S+8FeSO_4+4H_2SO_4$

In the production of the chalcocite from the bornite the reaction for cupric salts in the presence of oxygen may be as follows:

(11) $Cu_3FeS_3+CuSO_4+2O=2Cu_2S+FeSO_4+SO_2$

or, if oxygen be not present, the reaction may be:

(12) $5Cu_3FeS_3+11CuSO_4+8H_2O=13Cu_2S+5FeSO_4+8H_2SO_4$

For cuprous salt in the presence of oxygen the reaction is:

(13) $2Cu_3FeS_3+2Cu_2SO_4+2O=5Cu_2S+2FeSO_4+SO_2$

or, in the absence of oxygen:

(14) $8Cu_3FeS_3+11Cu_2SO_4+4H_2O=23Cu_2S+8FeSO_4+4H_2SO_4$

In all of the foregoing reactions the fundamental principle, so far as iron and copper are concerned, is the same. In every case the acid radical of the oxidized copper salt passes to the iron, and the sulphur in the iron unites with the copper, forming copper sulphide, thus producing a greater proportion of copper sulphide in the ore than before the reaction.

Too much stress must not be laid on the particular chemical reactions written. They are designed to show the nature of the reactions which may occur rather than to assert that the particular reactions written do occur exactly. It is believed that the reactions written are possible, but much experimental work must be done in the laboratory in order to ascertain which of the reactions is most common in an individual case. It is believed that the reactions for the production of rich sulphides of copper by descending waters are often those in which oxygen is present, but doubtless reactions without oxygen also take place frequently.

In all cases where SO_2 is regarded as produced by the reactions it may be that instead of this compound sulphuric acid is formed. Indeed, it is well known that SO_2 in the presence of ferric sulphate is oxidized to sulphuric oxide. In order to modify the equations in which SO_2 appears so as to produce sulphuric acid it is merely necessary to substitute H_2SO_4 for each SO_2 on the right side of the equation, and add H_2O+O on the left side. Probably the reactions in which oxygen is absent also occur in the first concentration of copper in consequence of the reactions of ascending copper solutions upon previously precipitated lower-grade materials.

While in some cases the sulphides were precipitated by reactions in which oxygen is present and in other cases by those in which it was absent, in still other cases I have no doubt that the reactions utilized some oxygen, but not as much as indicated by the equations as written. In such instances the real changes when precipitation took place are represented by equations which combine in various proportions those in which oxygen is represented as present and those in which it is absent. Moreover, for a certain part of a deposit the conditions may for a time have been those in which the reactions were without oxygen, later those in which it was insufficient, and finally those in which it was sufficient. Thus, all combinations of the reactions with and without oxygen may have taken place in the production of a single deposit.

The vertical relations of the richer sulphides which appear in passing from depth to the surface are very different in various regions. In some districts there may be somewhat regular gradations from the poor sulphurets at depth to the very rich sulphurets at or near the level of ground water. In other cases this change may be very abrupt. For instance, at Ducktown, Tenn., the lean cupriferous pyrrhotite changes rapidly into a zone of very rich sulphuret at and near the level of ground water. At Butte, Mont., the rich sulphurets are found at a much greater depth, and in the deeper workings of some of the mines secondary fracture openings in the lean sulphurets now contain small veins of rich sulphides of various kinds, even bornite or chalcocite, which have evidently been reduced by the lean sulphides adjacent. These illustrations show that the various sulphides overlap one another. In passing upward from the poor material, bornite may appear before the iron sulphide has been replaced largely by chalcopyrite, and at the place where bornite has become reasonably abundant chalcocite may be found. If the dominating material be iron sulphide, the copper mineral which is present is likely to be chalcopyrite rather than the richer sulphurets. Chalcopyrite is likely to be associated on the one hand with pyrite or pyrrhotite and on the other hand with bornite, or even chalcocite. Bornite and chalcocite are likely to be associated with each other and with chalcopyrite.

At still higher levels in a mine, a moderate distance below the level of ground water, oxidized and carbonated products may appear with the sulphurets. These mixed products, sometimes called oxysul-

phurets, are well illustrated in the Appalachian, Arizona, and Montana deposits.[a] Still higher, and especially above the level of ground water, the oxidized and hydrated products may become dominant, for there the rich sulphurets which have emerged from the ground water have been directly acted upon by the oxygen, carbon dioxide, and water. A series of transformations now take place which may result in metallic copper, cuprite, tenorite, azurite, and malachite, as already described. (See pp. 1158–1159.) The oxidized products may largely remain in place, furnishing rich ores, or they may be almost wholly dissolved and carried to lower levels, to react on the sulphides, as already explained.

Therefore rich sulphurets are first formed largely by the oxidation and the reaction of the oxidized products on lean sulphurets. Later, when in consequence of denudation, these rich sulphurets pass into the belt of weathering, rich oxidized compounds are produced. Thus in the upper few hundred meters of a vein there may be concentrated a large part of the copper produced by a first concentration in a much greater distance.

I do not mean to imply that each rich copper sulphide deposit has gone through the entire history above detailed, or that other factors have not been concerned in the development of the rich ore. Indeed, it will be seen that the general process outlined is much modified in many instances. (See pp. 1182–1189). However, it is held that processes of secondary concentration, due to descending water, have been very important factors in the production of rich copper deposits at many localities.

ASSOCIATION OF SILVER AND GOLD WITH BASE METALS.

The association of lead, zinc, and iron, and of copper and iron—two common cases—have now been considered. A similar set of transformations can be traced out in either of these classes of deposits when they contain silver and gold.

SILVER.

In the case of silver it is well known that the original forms are generally sulphides, sulphantimonites, sulphantimonates, sulpharsenites, sulpharsenates, and silver replacing a part of the iron, lead, zinc, or copper in the sulphides of these metals. Silver is one of the compounds which holds

[a] Douglas, James, The copper resources of the United States: Trans. Am. Inst. Min. Eng., vol. 19, 1891, p. 688–695.

strongly to sulphur. Ordinarily it is not sufficiently abundant to constitute the main mass of an ore deposit. Since silver holds so strongly to its sulphur, the silver salts are likely to be found, in the case of lead-zinc-iron compounds, most abundantly with the lead, less abundantly with the zinc, and least abundantly with the iron; and in the case of the copper-iron compounds, most abundantly with the copper and less abundantly with the iron. Native silver and the rich silver compounds—cerargyrite (AgCl), argentite (Ag_2S), proustite (Ag_3AsS_3), pyrargyrite (Ag_3SbS_3), and stephanite (Ag_5SbS_4)—may be found abundantly in the upper parts of mines, but frequently decrease in amount in passing from the surface to the zone of sulphides, and at sufficient depth in this zone may entirely disappear, the products being wholly argentiferous lead, zinc, copper, and iron sulphides. In many instances independent silver minerals do not occur at all, all of the silver being in the lead, zinc, copper, and iron compounds. In the argentiferous lead, zinc, and iron deposits, the ores are likely to contain less silver as they become poorer in lead and zinc. As the argentiferous copper deposits become poorer in copper with depth, the silver also ordinarily decreases in amount. Therefore the plumbiferous and zinciferous pyrites and cupriferous pyrites deep in the mines ordinarily contain less silver than the deposits above, which are richer in the base metals.

In the belt of weathering above the level of ground water native silver and silver chloride, cerargyrite, are likely to be found. The native silver is produced by the direct oxidation of the sulphur, antimony, or arsenic united with the sulphur. For instance, if the silver compound be Ag_2S, metallic silver is produced by simple oxidation of the sulphur as follows:

$$Ag_2S+O_2=2Ag+SO_2,$$

This reaction is very common, because silver is very slowly oxidized. But argentite may be directly oxidized to sulphate, according to the following reaction:

$$Ag_2S+2O_2=Ag_2SO_4.$$

This compound is a very readily soluble one, and therefore does not remain in situ, but if chlorides are present they react upon this salt and produce cerargyrite, according to the following reaction:

$$Ag_2SO_4+2NaCl=2AgCl+Na_2SO_4.$$

It is well known that in arid regions, native silver and cerargyrite are especially abundant in the belt of weathering. These compounds are produced in the same manner as native copper and its oxidized products, with, however, one additional factor. In arid regions the alkaline salts, such as sodium chloride and similar compounds, are segregated. (See pp. 542–543.) Therefore in such regions the ground waters are particularly likely to contain chlorides in solution which react upon the sulphates and thus produce the chloride of silver. Water is not sufficiently abundant to dissolve the chloride and hence cerargyrite accumulates.

Not all the silver which is oxidized to the soluble form of sulphate is precipitated as chloride, and even the chloride is somewhat readily soluble, so that if the silver be thus transformed a part of it may be held in solution. Therefore silver sulphate, and some silver chloride passes downward from the belt of weathering to the belt of sulphides. Since silver holds to its sulphur more tenaciously than any of the base metals with which it is associated, the first of the sulphides of these metals which is met in mass is reacted on by such silver salts. Where they may come into contact with chalcocite, for instance, argentite is precipitated according to the following reactions:

$$Cu_2S+Ag_2SO_4=Ag_2S+Cu_2SO_4.$$
$$Cu_2S+2AgCl=Ag_2S+2CuCl.$$

While it would be easy to write equations representing the reactions of the soluble silver salts upon the various sulphides of the base metals, producing silver sulphurets, it hardly seems worth while to do so until experimental work has determined the reactions which actually take place in the different cases. For the present purpose it is necessary only to understand that when soluble silver salts are brought into contact with base sulphides the silver certainly will be precipitated as independent silver sulphides or as rich sulphides in which the silver replaces a part of the base metals.

As an instance in which silver is concentrated in a base sulphide rather than in the carbonate of the base metal may be mentioned the Leadville ores. Here, according to Emmons, the galena is much richer in silver than the associated cerussite. Not only is this so in general, but there are some very interesting special cases. For instance, five assays of galena nodules which had carbonate crusts showed "six times as much silver in the galena

as in the cerussite."[a] Essentially the same phenomenon has been observed by Spurr in the Monte Cristo district of Washington. He says that here "the very richest ores in the district are the bunches of sulphides which are residual in the oxidized ores."[b] Such cases as these may be partly explained by the abstraction of the silver as sulphate from the lead carbonate, but I suspect it to be mainly explained by the reaction of the oxidized silver salts upon the galena, producing a galena richer in silver than originally existed.

Where the silver is largely changed to the sulphate and chloride, and is not largely precipitated as cerargyrite, the upper part of the silver veins in the belt of weathering may be greatly depleted in silver as a result of this leaching process. That the silver is not thrown down as cerargyrite may be due to a deficiency of chlorine in the descending solutions, or to the fact that the solutions are of such a character or so abundant that they are capable of dissolving the silver chloride. Illustrations of this process of depletion may probably be found in the Cripple Creek district, where the upper parts of the veins which carry free gold are deficient in silver, while the original telluride contains a certain amount of the latter metal, indicating that it has been leached out.[c]

GOLD.

It has already been fully explained (see pp. 1088–1089, 1139–1140) that gold occurs extensively (1) in the native form free from sulphides and tellurides; (2) in the native form closely associated with sulphides and tellurides; and (3) as a telluride. In the belt of weathering gold is very largely found in the metallic form, associated with the oxidized products of the base metals, especially with oxide of iron. Much of such gold was originally associated with the sulphides or the tellurides, or was united with tellurium as a telluride.

If the gold is in the metallic state, and merely inclosed in sulphides of iron or other sulphides, it is freed by the oxidation of these sulphides. Where it is united with tellurium it is necessary that this element be

[a] Emmons, S. F., Geology and mining industry of Leadville, Colo.: Mon. U. S. Geol. Survey, vol. 12, 1886, p. 553.

[b] Spurr, J. E., The ore deposits of Monte Cristo, Washington: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, p. 851.

[c] Penrose, R. A. F., jr., Mining geology of the Cripple Creek district, Colo.: Sixteenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1895, pp. 131–132.

oxidized in order that the free gold may be produced. This may take place first by the oxidation of tellurium to an oxide, and then the solution of the oxide by acids. Or the sum total of all the changes may be represented in a given case as follows:

$$Au_4Te_3+12NaCl+6CO_2+6O=4Au+3TeCl_4+6Na_2CO_3$$

That this or some similar process of the oxidation of the tellurium, leaving gold behind, has taken place upon an extensive scale at Cripple Creek, is shown by the very frequent pseudomorphs of spongy gold after the various tellurides.

The free-gold ores thus formed in the belt of weathering are commonly very much richer than the downward extensions of the deposits, in which the gold is associated with sulphides or tellurides, or occurs as a telluride. This exceptional richness of the upper part of the gold deposits is so well known that it is unnecessary to give many cases illustrative of it. However, one or two of the more important districts may be mentioned. In Australia, Don says, "for ounces per ton above the ground-water level, only pennyweights per ton have been found below it."[a] In the Sierra Nevada deposits, according to Lindgren, near the surface the values are from $80 to $300 per ton, whereas deeper they are somewhat uniform for the given vein, and run from $20 to $30 per ton.[b] In many instances the decrease in values is so great, in passing from the belt of weathering to the deeper workings, that while the belt of weathering and the upper part of the belt of cementation may be very profitable, the deeper portions of the deposits are so lean as not to warrant working.

These facts seem to me to be conclusive evidence that, in some way, the downward-moving waters have concentrated in a comparatively narrow belt an amount of gold which originally had a much wider vertical extent. That is to say, in some way, as denudation continued downward, the gold deposited in one of the original forms has been taken into solution by the descending waters and has been reprecipitated, thus producing the enriched upper part of the veins. As this process continues the belt of weathering becomes richer and richer, there being segregated within a comparatively

[a] Don, J. R., The genesis of certain auriferous lodes: Trans. Am. Inst. Min. Eng., vol. 27, 1898, p. 596.

[b] Lindgren, Waldemar: The gold-quartz veins of Nevada City and Grass Valley, California: Seventeenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1896, p. 128.

small vertical distance (from a few meters to 100 meters or more) a large part of the gold which, as a first concentration, may have had a vertical extent of 1,000 to several thousand meters.

It has been seen that gold is soluble in ferric chloride, cupric chloride, sodic carbonate, alkaline sulphides, and in other compounds. There are likely to be present in descending waters ferric chloride and ferric sulphate, and, in case the lode is a copper-bearing one, also cupric chloride. It is therefore believed that in the upper part of the belt of weathering these reagents or others take the gold in solution. As the solutions pass below the belt of weathering and into the belt of cementation they come into contact with sulphides of the base metals, tellurides, or organic materials, or are mingled with reducing solutions. It has already been seen that any of these conditions results in the precipitation of gold from its solutions, and therefore the gold is thrown down by these compounds in the upper part of the belt of cementation. Probably in the majority of instances the sulphides are the chief reducing compounds, although the others are not unimportant. The reduction of gold by sulphides is somewhat different from the reduction of any of the metals previously considered. Zinc, lead, copper, and silver are thrown down from their salts as sulphides by the baser sulphides. The gold is thrown down from its salts by those sulphides not as a sulphide but as metallic gold, because gold and sulphur have such weak affinity and gold is so easily reduced to the metallic form.

As denudation goes on the enriched upper portion rises into the belt of weathering. The sulphides and tellurides are there again oxidized, the gold is again partly dissolved and transported downward to be again precipitated, and thus an horizon of steadily increasing richness and breadth is formed below the belt of weathering in the belt of cementation, the gold commonly being largely free, but associated with sulphides.

During the process not all the gold which rises into the belt of weathering is dissolved, and the richer the sulphide zone which rises into the belt of weathering the greater the amount of gold left behind. This process of chemical concentration in the belt of weathering is supplemented to an important degree in many districts by residual concentration. As denudation continues the rocks are disintegrated, dissolved, and transported to the streams to a greater extent than is the gold, and thus the gold in the

upper parts of the veins is segregated. Segregation by this method is especially important at and near the surface. It thus appears that the production of the free gold of the upper parts of lodes is largely a chemical process, but is partly a process of residual concentration The two together continued for a sufficient length of time are believed to adequately explain the rich free gold ores of the upper parts of lodes.

Cripple Creek furnishes an excellent illustration of rich free gold at and near the surface. Near the surface numerous deposits in this district were exceptionally rich, containing a large amount of free gold above and near the level of ground water. Usually much of this free gold was in spongy pseudomorphs after tellurides, showing its formation in large measure by the direct oxidation of the tellurium of the tellurides, the gold being left behind. For some years it has been well known that below the upper belt of rich material in many of the veins the deposits were very much poorer. Indeed, many of the deposits were found to be so poor below the upper narrow belt of rich ores as to lead to their abandonment.

In reference to this poor ground Mr. Moore says:

"It is undoubtedly true that some mines have entered poor ground in the veins at depths of 250 feet [75 meters] to 400 feet [120 meters] below the surface, and have sunk down to depths of 400 feet [120 meters] to 500 feet [150 meters] deeper without finding payable ore bodies again." But this was by no means true of all the deposits. Mr. Moore further says, "It is a fact that in a greater number of mines the values have been carried down to more than 1,200 feet [360 meters] below the surface continuously, and in at least two mines the values have greatly increased from 1,100 feet [330 meters] downward."[a] A most interesting feature in reference to the Cripple Creek district has been developed recently. Deep in some of the mines which showed a depleted horizon there has been discovered a lower horizon of very rich ores, partly sulphides and tellurides, but also in large part free gold.

According to Mr. Hills: "The original ground-water level at Cripple Creek is about altitude 9,500 feet [2,850 meters] for the west side of the district and considerably higher for the Bull Cliff region."[b] The upper part

[a] The Daily News, Denver, Colo., Jan. 1, 1903, p. 3.

[b] Ninth Ann. Rept., Portland Gold Mining Co., Victor, Colo.; Report of Victor G. Hills, Consulting Engineer, 1903, p. 87.

of these rich deposits appeared upon an average at least 120 meters below ground-water level. Mr. Moore[a] states that the depths of the deepest shafts in the Cripple Creek district vary from 240 to 450 meters. On Battle Mountain are the Portland, Granite, Burns, Ajax, Stratton's Independence, Strong, Gold Coin, and Modoc. At Bull Hill are the Last Dollar, Blue Bird, Logan, American Eagles, Wild Horse, Isabella. At East Spur Bull Hill are the Independence T. & M. Co., Vindicator, Lillie, and Golden Cycle. He says in reference to these deposits: "All but one of these shafts have good bodies of ore and excellent indications for the future at the lowest levels to which they have thus far attained. Certain of these shafts, to wit, the Last Dollar and Blue Bird, show some of the richest ore ever mined in the district at their lowest levels." Mr. Moore regards these deep, rich deposits as due to the secondary action of descending waters. It has already been noted that in the Cripple Creek districts the values in the upper part of the veins near the ground-water level are very largely in native gold; deeper they are largely in the tellurides, the sulphides being comparatively poor; while still deeper they are to a large extent in the sulphides.

If these are facts they seem to be evidence that the ores of the Cripple Creek district have undergone two concentrations. The first concentration was by ascending waters, and the ores were originally deposited in some measure as tellurides, but perhaps more largely as free gold associated with sulphides. In consequence of later denudation, with action by descending waters, secondary segregation may have taken place and produced two rich upper horizons, that of free gold largely above the level of ground water and that of the rich tellurides and associated free gold, mostly below it.

Exceptionally the Cripple Creek mines have a deep horizon of rich tellurides. In most districts where rich ores occur at some depth below the level of ground water the reduction of the gold to its free state is believed to be largely the work of the base sulphides. As already noted, in the deeper workings of the Cripple Creek district the values are largely in the sulphides, and the tellurides are subordinate. The natural explanation of the rich tellurides is that as the original sulphides and tellurides rose above the level of ground water the gold and tellurium were both

[a] The Cripple Creek Times, December, 1902.

oxidized and traveled down, the first as gold chloride or a similar salt, and the tellurium as telluric chloride or a similar salt. Below the level of ground water these two compounds would both be reduced where they came into contact with the base sulphides. At the moment of reduction they may have united, and thus the rich tellurides of gold may have been formed. It is thought possible that precipitation was caused in this manner rather than by previously existing lean tellurides of the first concentration, because in the deeper workings of some of the mines the tellurides seem to be very subordinate to the sulphides, and the values are mainly in the sulphides. If the above suggestion proves correct, in the Cripple Creek district the deep, rich tellurides represent a concentration of tellurium as well as of gold. If the amount of tellurium for the upper 500 meters or more of the lodes was not originally greater than in the deeper workings, the tellurium now found in the deep rich horizon must have had a much wider original vertical distribution.[a]

The formation of the rich free gold near and above the level of ground water in the Cripple Creek district is not materially different from the formation of such products elsewhere. As denudation continued the enriched sulphides and tellurides rose above the level of ground water, the sulphur and tellurium were there oxidized, and some of the free gold was left behind. This chemical process was accompanied by residual concentration.

CONCENTRATION BY REACTION UPON SULPHIDES COMPARED WITH METALLURGICAL CONCENTRATION.

One of the more common processes of metallurgy for the separation of gold, silver, copper, and lead from iron is based upon the principle explaining the second concentration given on preceding pages, viz, that iron holds sulphur less strongly than the other elements named. The sulphureted ores are imperfectly roasted, thus partly oxidizing them to oxides and sulphates. The ores are then smelted in a furnace with a flux. The oxides of the valuable metals and the sulphates react on the remaining sulphides of all the metals, producing a matte containing the sulphides of the valuable metals. The iron gets all or nearly all of the oxygen; the iron oxide unites with the fluxes and passes into the slag.

[a] Since the above was in page proof I have been informed by Dr. Lindgren, who has closely studied the district, that he doubts the existence of enriched deep tellurides at Cripple Creek. If these tellurides do not exist the two preceding paragraphs need radical modification.

OTHER REACTIONS OF DESCENDING SOLUTIONS.

In the foregoing pages the second concentration of metals by solution, downward transportation, and precipitation by reactions on the sulphides of the first concentration has been emphasized. However, it is not supposed that this is the only process which may result in enrichment by descending waters of the upper parts of vein deposits. The enrichment of this belt may be caused by reactions between the downward-moving waters carrying metallic compounds and the rocks with which they come in contact, and by reactions due to the meeting and mingling of ascending and descending waters.

The descending waters carrying metals dissolved in the upper part of the veins may be precipitated by material contained in the rocks below. This material may be organic matter, ferrous salts, etc. So far as precipitating materials are reducing agents, they are likely to change the sulphates of most of the metals to sulphides, and precipitate the metals in that form. While sulphides may thus be precipitated to some extent above the level of ground water, because of the deficiency of oxygen they are thrown down much more largely below it. The reducing solutions ordinarily precipitate gold from its solutions in the metallic form.

In a trunk channel, where ascending and descending waters meet, there is a considerable horizon in which the circulation is slow and irregular, the currents now moving slowly upward and now moving slowly downward, and at all times being disturbed by convectional movements. Doubtless this belt of slow general movement and convectional circulation reaches lower levels at times and places of abundant rainfall than at other times and places, for under such circumstances the descending currents are strong. The ascending currents, being controlled by the meteoric waters falling over wider areas, and subject to longer journeys than the descending currents, do not so quickly feel the effect of abundant rainfall. Later, the ascending currents may feel the effect of the increased rainfall and carry the belt of upward movement to a higher level than normal. However, where the circulation is a broad one, little variations in ascending currents result from irregularities of rainfall.

In the belt where ascending and descending waters meet (see fig. 26), convectional mixing of the solutions due to difference in temperature is an important phenomenon. The waters from above are cool and dense, and

tend to sink downward, while those from below are warm and less dense and tend to rise; thus the waters are mingled. But even if the water were supposed to be stagnant at the neutral belt, it is probable that by diffusion the materials contributed by the descending and ascending waters would be mingled.

Ascending and descending solutions are sure to have widely different compositions, and an accelerated precipitation of metalliferous ores is a certain result of their mixture. As an illustrative case in which precipitation is likely to occur, we may recall that ascending waters contain practically no free oxygen, frequently contain hydrogen sulphide, and are often somewhat alkaline, while descending waters are usually rich in oxygen and frequently contain acids, as at Sulphur Bank, described by Le Conte.[a] The mingling of such waters as these is almost sure to result in precipitation of some kind. As illustrating the effect of the mingling of descending and ascending solutions we may suppose that the sulphides of any of the metals are rising in solutions of sodium sulphide, and that the descending waters are carrying sulphates of the metals and sulphuric acid. The sulphuric acid would destroy the sodium sulphide according to the following reaction:

$$Na_2S+H_2SO_4=Na_2SO_4+H_2S$$

The sodium sulphide being destroyed, the sulphides traveling as such in the ascending solutions would be thrown down. This reaction also produces hydrogen sulphide, which, formed in this way or originally present, would throw down metals from the descending oxidized salts. For instance, sulphate of copper would be thrown down as a sulphide by hydrogen sulphide. Another illustrative case is the mingling of descending waters bearing oxygen with ascending waters bearing iron carbonate. The result is to throw down the iron as ferric oxide, according to the following reaction:

$$2\,FeCO_3+O+nH_2O=Fe_2O_3\,.\,nH_2O+2CO_2$$

Le Conte also suggests that by the mingling of the waters from below with those from above the temperature of the ascending column is rapidly lessened, and this also may result in precipitation. The dilution may work in the same or in the reverse direction.

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[a] Compare Le Conte, Am. Jour. Sci., 3d series, vol. 24, 1882, p. 33, and vol. 26, 1883, p. 9.

The metals precipitated by the mingling of waters may be contributed by the descending waters, by the ascending waters, or partly by each. In so far as more than an average amount of metallic material is precipitated from the ascending waters, this results in the relatively greater richness of the upper part of veins independently of the material carried down from above.

The above methods of precipitation and enrichment of the upper parts of deposits follow from the reactions of downward-moving waters. Their effect is to precipitate the metals of the ascending water to some extent, and thus assist in the first concentration. But the results of these processes can not be discriminated from the second concentration, which is caused by an actual downward transportation of the material of the first concentration. It is believed that the peculiar character of the upper portions of lodes is mainly owing to downward transportation of metals previously precipitated (see pp. 1182–1189); but whether this be so or not, it is certainly due to descending waters.

SECOND CONCENTRATION FAVORED BY LARGE OPENINGS NEAR THE SURFACE.

The concentration of large ore bodies in the belt of weathering and in the upper part of the belt of cementation is greatly favored by the abundance and size of the openings as compared with the openings at greater depths.

The openness of the rocks above the level of ground water and the rapid lessening of the volume of the openings below it have already been alluded to as general phenomena, and an explanation has been offered that in the belt of weathering solution is the law, and in the belt of cementation cementation is the law. (See pp. 484–487, 562–565, 612–617.) Of course, it is understood that there is usually not a sudden change in the amount of pore space at the level of ground water, but at and below it the extremely open upper ground grades into the much less open lower ground. In some instances the gradation requires some distance. Thus, so far as the openings are concerned, the conditions for the formation of large ore deposits are more favorable above the level of ground water and as far below it as openings are numerous than at deeper levels.

This openness of the belt of weathering and the comparative closeness of the belt of cementation are well illustrated by many limestone regions;

for instance, the lead and zinc district of southwestern Wisconsin, already described. (See pp. 1144 et seq.) Another excellent illustration of very loose and open ground above the level of ground water and tight ground below it is furnished by the Monte Cristo district of Washington.[a] Here near the surface all the minor joints are open, circulation has been free, and the larger ore deposits are found. At depth the joints are mostly tight, only a few being sufficiently open to allow of much water circulation.

But numerous and large openings may exist below the level of ground water. In various kinds of rocks—such as sandstones, conglomerates, amygdaloids, and tuffs—the openings are original, and may not have been closed by cementation. Of course, the more recent the earth movements the more numerous and larger are the openings. In some places the descending waters are not saturated when they reach the level of ground water, and solution continues for some distance below it. Furthermore, the level of ground water varies under different circumstances. Where a region is being uplifted the level of ground water, other things being equal, is descending, and where a region is subsiding it is rising. As a result of physiographic changes there may be alternate valley filling and valley erosion. These changes affect the level of ground water. In Pleistocene time there was an extensive period of valley filling instead of erosion. Consequent on this the level of drainage, and therefore the level of ground water, rose. Also there may be very considerable variations in the level of ground water as a consequence of long-continued climatic changes, such, for instance, as the alternating periods of humidity and aridity in the Cordilleras of the West in connection with the Pleistocene.[b] To illustrate, at the present time in the mining districts of New Mexico and Arizona the level of ground water is far below the surface, but it can not be doubted that during the humid epoch evidenced by the existence of Lake Bonneville and Lake Lahontan the level of ground water was much higher. Emmons gives a specific case in which the ground water was apparently once nearer the surface than at present. According to him, at the Delamar

[a] Spurr, J. E., The ore deposits of Monte Cristo, Washington: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, p. 847.

[b] Gilbert, G. K., Lake Bonneville: Mon. U. S. Geol. Survey, vol. 1, 1890. Russell, I. C., Geological history of Lake Lahontan, a Quaternary lake of northwestern Nevada: Mon. U. S. Geol. Survey, vol. 11, 1885.

mine the lower levels are as dry as the upper levels. The region is arid and the mine is never wet, but the mine shows "universal evidence of a secondary enrichment that must have proceeded from the surface downwards."[a] This fact Emmons regards as evidence that at the comparatively recent Bonneville epoch the water level was comparatively near the surface.

Aside from secular changes in the level of ground water, due to variations in rainfall extending through geological periods, the shorter periods of varying rainfall produce some effect upon the level of ground water. Thus the annual and several-year period variations in rainfall cause slight changes in it.

All these changes favor alternate solution and deposition—solution when the level of ground water falls, precipitation when it rises. Where the ground water has been at a low level large openings to some depth are likely to be produced. Where later for some reason the level of ground water rises these openings are in a very favorable position to be filled with ore, as a result of precipitation from ascending solutions, of the reactions of descending solutions, and of the mingling of ascending and descending waters.

It might be argued that the existence of ore deposits in the large openings of the belt of weathering is evidence that the ores were not first deposited by ascending waters. However, as has been already explained, in such openings there may be concentrated mineral material originally distributed by ascending waters through a much greater vertical distance. Thus a very rich ore deposit in large openings, formed by the reaction of descending waters upon a first concentration produced by ascending waters, may be bounded below by a horizon in which the ground is very close, the comparatively small openings which once existed having been greatly enlarged by solution during reconcentration by descending water.

DEPTH OF EFFECT OF DESCENDING WATERS.

There can be no doubt of the importance of downward-percolating waters in the production of ore deposits in the zone in which they are active. The only question which remains open is the depth to which they are effective. This varies greatly in different districts and in the mines of

[a] Emmons, S. F., The Delamar and the Horn-Silver mines; two types of ore deposits in the deserts of Nevada and Utah: Trans. Am. Inst. Min. Eng., vol. 31, 1902, pp. 672–673.

the same district. In general, the effect is likely to be deep seated in proportion as the lode worked is on high ground. (See p. 1181.)

In arid regions the level of ground water is far below the surface and the process of denudation is slow, so that the downward-moving waters have both a wide belt in which to work above the level of ground water and a long time in which to work upon a given horizon. In such regions the oxides and carbonates are likely to occupy a considerable horizon. This is very well illustrated by the copper mines of Arizona and New Mexico and by the "colorados" of the silver-gold deposits in various arid regions.

In humid regions, on the other hand, the level of ground water is likely to be near the surface. If this be combined with marked relief so that denudation is rapid, the processes of oxidation and carbonation may be very incomplete above the level of ground water. Indeed, in many cases erosion may be so rapid that the sulphurets do not have time for more than very partial oxidation, and they may extend nearly or quite to the surface. If the rainfall is abundant, descending waters are likely to be effective below the level of ground water; and if there are large openings and strong relief, the waters are effective to a considerable depth. Consequently even where there are no oxidized products above the level of ground water, the ores are likely to have been enriched by descending waters in the belt of cementation. It is very seldom that a deposit is found in which no effect of descending waters can be discovered.

It has already been seen that the level of ground water may vary from the surface to a depth of 300 meters or more. Hence it is certain that from the surface to a depth of 300 meters the ground waters may be a potent factor in the production of the rich ore deposits. The deposits in this belt are particularly profitable, not only because of the accessibility of the material, but because of the fact that there is no expense for pumping; furthermore, the products are commonly easily reducible. This may be illustrated by the gold and silver deposits. In the former, the native gold is free from its entanglement of sulphurets and tellurides; in the latter the silver is largely in the form of the readily extracted chloride, or in some instances as native silver. Aspen Mountain furnishes an excellent illustration of a broad belt of weathering. Here, at a depth of 250 meters, at least one great body of lead carbonate has been developed. This carbonate contains a few small crystals of galena, showing its derivation from the sulphide, and

therefore showing that the oxidizing, carbonating waters above the level of ground water have been extremely effective.

Up to this point there will be no disagreement on the part of anyone. The question now arises as to the depths below the level of ground water to which descending waters produce their effects. This is a question to be answered, not by deduction, but by observation. Even Posepny, who emphasizes the effect of ascending waters, agrees that oxidized products are the evidence of the work of vadose circulation, or the circulation of lateral and downward-moving waters. Furthermore, Posepny agrees that the iron ores of the Lake Superior region,[a] which are oxidized products, have been produced by downward-moving waters. A number of the mines have been worked to a depth of 500 meters or more below the level of ground water; and in these cases it is perfectly clear that to this depth the downward-percolating waters have produced an oxidizing effect. This is true in a region in which the level of ground water is relatively near the land surface, and which is not mountainous. In various other regions oxidized products are found also to a very considerable depth below the level of the ground water.

In the San Juan district of Colorado, in the Revenue tunnel of the Virginius mine, the effect of oxidizing waters has been observed to the depth of nearly 1,000 meters, as shown by iron-oxide stains through the sulphides. How much deeper oxidation may be effective is not known, and below this depth there may be a belt in which the sulphides may have been enriched by descending solutions from above without the actual production of oxidized products. In the Cripple Creek district of Colorado oxidized products are not found to a great depth, but if the suggestion is correct that the high-grade tellurides are due to the effect of descending waters, such waters must have been effective to a depth of 400 meters. As yet the lowest limits of the enriched belt has not been reached, and how much deeper it extends is unknown. Both these districts are humid and of very accentuated topography, and thus furnish exceptionally favorable conditions for descending waters to produce deep effects.

The illustrations given furnish positive evidence that the belt in which descending waters are effective in producing rich secondary concentrates under favorable conditions extends to a very considerable depth.

[a] Posepny, F., Genesis of ore deposits (discussion): Trans. Am. Inst. Min. Eng., vol. 24, 1895, pp. 966–967.

ILLUSTRATIONS OF SECONDARY ENRICHMENT AND DIMINUTION OF RICHNESS WITH DEPTH.

The processes have now been explained by means of which a rich upper belt may be produced. If the argument be correct, it is an inference from this that ore deposits which have undergone a second concentration are likely to diminish in richness with depth, provided a considerable belt be considered. It remains to give the facts which confirm the above hypothesis, and illustrate diminution of richness with depth.

At Ducktown, Tenn., at the level of ground water, appeared a belt of rich black copper ore (copper glance), which varied from less than 1 to about 2½ meters in thickness. Above this belt was gossan, very poor in copper; below it a very low grade cupriferous pyrrhotite.[a] In this instance it can hardly be doubted that originally the lean cupriferous pyrrhotite extended not only to the present surface but probably much higher. The downward-moving waters transported copper to its locus near the level of ground water. Here the copper salts reacted on the iron sulphide and produced rich sulphurets.

A case which has been, perhaps, more closely studied than any other in the United States is that of the deposits of Butte, Mont. Douglas states that here rich oxysulphurets are found near the surface. On the summit of the hill "it seems as if the copper, leached out of the 400 feet (120 meters) of depleted vein, had been concentrated in the underlying ore, and had thus produced a zone of secondary ore about 200 feet (60 meters) deep, which contains, as might be expected, about thrice its normal copper content."[b] Of the Butte deposits Emmons says:

> Secondary deposition, or transposition of already deposited minerals, has played an unusually important rôle. In the case of the copper veins it has not been confined to the oxidizing action of surface waters, which has resulted in an impoverishment of the ore bodies, but below the zone of oxidation it has resulted in the formation of the richer copper minerals bornite, chalcocite, and covellite, in part, at least, by the breaking up of original chalcopyrite. Unusual enrichment of the middle depths of the lodes has thus been caused. Whether the two processes of impoverishment and enrichment have been differing phases of the action of descending waters, or whether the latter may have been a later result of the rhyolite intrusion, has not yet

[a] Blake, W. P., The persistence of ores in lodes in depth: Eng. and Min. Jour., vol. 55, 1893, p. 3. Henrich, C., The Ducktown ore deposits and the treatment of the Ducktown copper ores: Trans. Am. Inst. Min. Eng., vol. 25, 1896, pp. 206–209.

[b] Douglas, James, The copper resources of the United States: Trans. Am. Inst. Min. Eng., vol. 19, 1891, p. 693.

been definitely decided. It is, however, fairly well determined that the enrichment of the copper deposits is so closely associated with the secondary faulting that it may be considered to be a genetic result of it.[a]

While the larger and richer sulphide bodies were found at from 60 to 125 meters below the water level, rich sulphide bodies of smaller size are here and there found at a depth of 450 meters below the water level, "though in apparently decreasing amount as compared with the immense thickness of pyritous ore."[b] Brown states that in the same area oxidized products extend to the level of ground water. These oxidized products, according to Brown, promptly change at water level into normal sulphurets. "There follows below a region of varying height, of valuable rock, which again slowly deteriorates in depth, this deterioration, however, being so retarded finally as to be scarcely appreciable."[c] He further says that above the level of ground water is gossan "carrying high values in silver, and particularly in gold."[d] Thus at Butte we have enrichment in silver and gold and depletion in copper in the belt above the level of ground water as compared with the material below it; and at and below the level of ground water we have rich sulphides of copper which grade into leaner sulphurets. In the case of the Butte deposits it can hardly be doubted that the comparatively lean sulphides in the deeper workings represent the product of a first concentration, and that the modifications of this material found above and below the level of ground water represent the work of downward-moving waters. To account for the high values of gold and silver above the level of ground water, one must suppose that this belt has received contributions of these metals from the upward extension of the veins which has now been removed by erosion. The great richness of the copper below the level of ground water Douglas clearly attributes to the downward transportation of the material from the depleted copper veins. However, a part of this material was doubtless derived from an upward extension of these veins, precisely as in the case of the gold and silver. For my own part, I have little doubt that the precipitation of the rich sulphides was produced by reactions upon the lean sulphurets, as given in the equations on pages 1161–1164.

[a] Emmons, S. F., Economic geology of the Butte special district, Montana: Geologic Atlas U. S., folio 38, 1897.

[b] Emmons, S. F., The secondary enrichment of ore deposits: Genesis of ore deposits, Am. Inst. Min. Eng., 2d ed., 1902, p. 444.

[c] Brown, R. C., The ore deposits of Butte City: Trans. Am. Inst. Min. Eng., vol. 24, 1895, p. 556.

[d] Brown, cit., p. 555.

Penrose cites the Arizona copper deposits as instances of secondary concentration. These deposits he regards as produced by leaching of the copper from a lean copper-bearing pyrite, and its segregation at the places where the rich ores occur. In this process Penrose, however, says that the volume of the deposit must be decreased; but he makes the point that the smaller amount of the rich product is more valuable than a larger lean deposit, because more easily mined and more readily reduced.[a] This process of concentration is further described by Douglas, who notes, also, that the changes have resulted in the production of enriched sulphides from very lean sulphides in the Copper Queen mine. Here, according to Douglas, a large very low-grade copper-bearing pyrite deposit running from the 60- to the 120-meter level contains rich oxysulphides and black sulphides on the outside and mainly lean pyrite in the interior.[b] The original material in the Arizona locality is as plainly a lean cupriferous pyrite as in Tennessee. Here, however, on account of the peculiar climatic conditions, the alterations have been of a different kind and have not extended to a uniform depth. Instead of the rich belt being a horizontal sheet, it occurs in a zone about a large cupriferous pyrite mass; but the principles of concentration are identical, and the rich products are unquestionably in part due to reactions between the oxidized salts and the lean sulphides. The rich oxidized products of the Southwest doubtless were produced directly from the enriched sulphurets. Therefore, in the formation of the rich oxidized products there were two stages of alteration; first, the production of rich sulphurets by the reaction of oxidized products upon the lean pyritiferous material, and after that oxidation of the rich sulphurets. These oxidized ores formed partly in situ, but there has been also more or less of transfer of material from one place to another.

An excellent illustration of an enriched upper belt in the case of gold is furnished by the gold-quartz veins of Grass Valley, California, where, according to Lindgren, the decomposed belt of weathering, about 50 meters in depth, contains "from $80 to $300 per ton, while the average tenor in depth is from $20 to $30."[c] Furthermore, the rich 50 meters, which con-

[a] Penrose, R. A. F., jr., The superficial alteration of ore deposits: Jour. Geol., vol. 2, 1894, pp. 306–308.

[b] Douglas, James, The Copper Queen mine, Arizona: Trans. Am. Inst. Min. Eng., vol. 29, 1900, pp. 532–533.

[c] Lindgren, Waldemar, The gold-quartz veins of Nevada City and Grass Valley, California: Seventeenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1896, p. 128.

tain from four to ten times as much gold as the sulphurets below the level of ground water, are depleted in silver. In some veins the sulphurets extend almost to the surface. Lindgren further states that the sulphurets below the level of ground water continue with undiminished richness to a depth of 500 or more meters.[a] He adds that the California region is one in which denudation has extended to a depth of 500 to 1,500 or more meters.[b] From these facts it is highly probable, as suggested by Lindgren, that sulphurets similar to those below the level of ground water were deposited above the present surface. If this were the case the only possible explanation of the belt of weathering rich in gold and depleted in silver is that descending waters have abstracted a large part of the gold from the material removed by erosion, and have deposited it in the belt of weathering. Its precipitation there was, doubtless, mainly due to reduction by the sulphides, producing sulphurets richer in gold. Later, the sulphides have been oxidized, leaving the enriched belt of free gold. The silver apparently has been transported downward to a greater extent. One would expect that correlative with the belt above the level of ground water poor in silver, there would be a belt at and below the level of ground water richer in silver. Upon this point Lindgren does not give us information.

Another very interesting case of richness of the belt of weathering in gold, as compared with the unaltered sulphides below, is furnished by the Australian gold fields, where the belt above the level of ground water is several times as rich as the unaltered tellurides and sulphides below; some mining men say ounces above to pennyweights below.[c] This rich belt is from 15 to 120 meters wide. In a portion of the mines of some districts—for example, the Kalgoorlie district—when the bottom of the oxidized zone is reached, the ores are so lean as to be valueless, so that mines which were profitable in the weathered zone did not pay below it.[d] Many of the mines of that district, however, are profitable below the weathered horizon. If it had not been for the secondary enrichment by denudation and downward transportation of material, many of the mines would not have been exploited,

[a] Lindgren, cit., pp. 161–163.

[b] Lindgren, cit., pp. 182–183.

[c] Don, J. R., The genesis of certain auriferous lodes: Trans. Am. Inst. Min. Eng., vol. 27, 1898, p. 596.

[d] Hoover, H. C., The superficial alteration of western Australian ore deposits: Trans. Am. Inst. Min. Eng., vol. 28, 1899, pp. 762–764.

although Hoover thinks that in this strange country the downward concentration is more mechanical than chemical. Thus the secondary concentration by descending waters is no less an important part of the genesis of the gold ores of Australia than the first concentration by ascending waters.

It has already been fully explained (p. 1144 et seq.) that the lead and zinc deposits of the Mississippi Valley furnish clear cases of the importance of the action of descending waters in enriching ores first concentrated by ascending waters.

The Leadville deposits furnish an instance of the decrease of the richness in silver with depth. Emmons says: "There is a fair foundation for the generalization that in the deposits, as developed at the time of this investigation, the ores were growing poorer in silver as exploration extended farther from the surface."[a]

The ores early mined contained scarcely any zinc. Emmons states of the ores of the deeper levels later mined that the "sulphide ores consisted of mixtures of pyrite, galena, and zinc blende, the latter in fairly equal amounts." The sulphide bodies immediately below the belt of oxidation are richer in zinc blende than the ore at greater depth. The material rich in zinc below correlates with the ores low in zinc near the surface, the zinc sulphide of that horizon having been oxidized, and the zinc carried down and redeposited.[b]

Another case of the diminution of the richness of sulphurets with depth is furnished by the nickel mines of Lancaster Gap, Pennsylvania, which were not worked beyond a depth of about 75 meters, presumably because "the ore decreased in richness as depth was attained."[c]

The San Juan district of Colorado gives excellent illustrations of decrease of values with depth. The upper parts of the lodes were usually very rich in silver, not infrequently ores running 300 ounces or more per ton. In the deeper workings of the veins the values in silver usually ran down, in many cases very rapidly, so that, at a depth of a few hundred meters the amount of silver became so low that work upon many of the

[a] Emmons, S. F., The geology and mining industry of Leadville, Colo.: Mon. U. S. Geol. Survey, vol. 12, 1886, pp. 554–555.

[b] Emmons, S. F., The secondary enrichment of ore deposits: Genesis of ore deposits, Am. Inst. Min. Eng., 2d ed., 1902, pp. 439–440.

[c] Kemp, J. F., The nickel mine at Lancaster Gap, Pennsylvania: Trans. Am. Inst. Min. Eng., vol. 24, 1895, p. 626. Discussion by E. E. Olcott, p. 884.

lodes ceased comparatively early in the history of the district. Regarding these ores Ransome says:

> In spite of the diversity shown by the different ore bodies, there is after all remarkable uniformity to be found in the change at very moderate depths—usually less than 300 feet [91 meters]—from an ore consisting chiefly of argentiferous galena to highly argentiferous silver-copper ores, and then a gradual diminution of value downward through the increasing proportion of low-grade pyrite in the ore bodies. These changes are best recorded in the Yankee Girl, Guston, and Silver Bell mines.[a]

In some of the deeper lodes of the district the values have become so low that they do not warrant working. While in some lodes there has also been a decrease in the amount of gold with depth, the gold values in general have held up very much better than the silver, and in some of the mines at a depth of 500 or more meters below the surface, as at the Camp Bird, the values are still very high in gold. Possibly the explanation of the difference between the two metals is that from the descending solutions the silver was thrown down more rapidly than the gold. Since silver is precipitated as a sulphide, it is very quickly thrown down from its soluble salts in consequence of the reaction of the sulphides of the base metals, such as galena, sphalerite, and pyrite; whereas by these compounds the gold is thrown down from its solutions in metallic forms, and is therefore probably more slowly precipitated, and consequently secondary enrichment extends much deeper.

The Monte Cristo district of Washington, described by Spurr, gives a most excellent illustration of the principle of decreasing richness with depth. In that district there is a definite arrangement of the ores vertically, which arrangement has a very marked relation to the topography. The order downward is, (1) oxidized ores; (2) upper sulphide belt, characterized by galena, blende, and chalcopyrite, carrying the highest values in gold and silver and extending not more than 100 meters below the surface; (3) intermediate sulphide zone, having reduced amounts of galena, blende, and chalcopyrite, and with these realgar, arsenopyrite, pyrite, and pyrrhotite; and (4) lower sulphide zone, low in gold and silver, and consisting of pyrite, pyrrhotite, and arsenopyrite, and in which galena and blende are subordinate or absent.[b] In the upper sulphide belt the "galena

[a] Ransome, F. L., A report on the economic geology of the Silverton quadrangle, Colorado: Bull. U. S. Geol. Survey No. 182, 1901, pp. 111–112.

[b] Spurr, J. E., The ore deposits of Monte Cristo, Washington: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, pp. 841–857.

zone is shallowest and is overlapped by the blende zone, and this by the chalcopyrite zone."[a] Thus in this upper belt there is a definite order of prominence of these three minerals—galena, blende, and chalcopyrite.

In addition to these specific instances of the production of a rich upper belt, some general statements have been made which need to be referred to. One of these is made by Douglas in reference to sulphuret mines as a whole. Says he, in the conclusion of his discussion as to the copper resources of the United States, with reference to the various Appalachian deposits, "Like all sulphuret mines, they became poorer as depth was attained."[b]

With the exception of the San Juan and Monte Cristo districts, the above illustrations of secondary enrichment and diminution of richness with depth are the same as originally published by me.[c] Recent articles by other authors have given many other instances of secondary enrichment which fall in line with the above illustrations, but which in this treatment of principles need not be repeated. Some of the more notable contributions upon this subject are those by Emmons,[d] Weed,[e] Ransome,[f] and Bain.[g]

Upon the hypothesis that the rich ores of the upper parts of deposits usually result from secondary action of descending solutions upon material no richer than the deeper parts of the deposits, the extent and richness of such deposits may give an approximate idea of the minimum denudation which a district has suffered. For example, at Ducktown, Tenn., to produce the rich oxidized products of copper above the level of ground water, and the very rich sulphides at and near it, from the lean, cupriferous pyrrhotite below, which bears about 2 per cent of metallic copper,

[a] Spurr, cit., p. 841.

[b] Douglas, James, The copper resources of the United States: Trans. Am. Inst. Min. Eng., vol. 19, 1891, p. 694.

[c] Van Hise, C. R., Some principles controlling the deposition of ores: Trans. Am. Inst. Min. Eng., vol. 30, 1901, pp. 128–134.

[d] Emmons, S. F., Secondary enrichment of ore deposits: Trans. Am. Inst. Min. Eng., vol. 30, 1901, pp. 177–217.

[e] Weed, W. H., Enrichment of mineral veins by later metallic sulphides: Bull. Geol. Soc. Am., vol. 11, 1900, pp. 179–206.

[f] Ransome, F. L., Ore deposits of the Rico Mountains, Colorado: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, pp. 229–397. Report on the economic geology of the Silverton quadrangle, Colorado; Bull. U. S. Geol. Survey No. 182, 1901, pp. 265.

[g] Bain, H. F., with Van Hise, C. R., and Adams, Geo. I., Preliminary report on the lead and zinc deposits of the Ozark region: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, pp. 23–227.

there must have concentrated in the shallow deposits at the surface an amount of copper which was originally distributed through a vertical distance of hundreds of meters. At Butte, Mont., the production of the rich sulphide deposits characteristic of that district must also have required enormous denudation. In this case where the belt of weathering is depleted in copper, it may be supposed that during the secondary concentration the major part of the copper originally distributed through a great vertical distance was carried downward and reprecipitated; and that the losses in consequence of denudation were not great. But in other cases, where geological studies show that great denudation must have taken place, the amount of enriched material is comparatively small. For example, in the Sierra Nevada gold belt, the enriched product has a thickness of not more than 30 meters and is not more than five times as rich upon the average as the sulphides of the first concentration below. It would therefore follow that the gold distributed through 150 meters of the first concentration would be sufficient to account for all of the enriched product, but Lindgren places the extent of the denudation in this district as about 3,000 meters. Hence in this case but a small part of the gold has been taken into solution by descending waters and transported below and reprecipitated. It therefore follows that the larger part of the gold produced by the original concentration has been carried away from the fissures by the processes of denudation, and correlative with these great losses to the veins are the placer deposits of California. While the material was mainly carried away from the veins, it was in great measure segregated in the beds of streams, past and present, from which deposits it is being extracted.

These instances of the relation of depth of denudation and amount of enriched deposits, where the evidence seems to be particularly clear, are mentioned with a view of suggesting an interesting line of study with reference to ore deposits rather than with an idea of giving exact or comprehensive data upon the subject.

GENERAL STATEMENTS.

It is believed to be a very general rule, if a long enough scale be used, that ore deposits diminish in richness with depth. But it is well known that above the level of ground water the valuable materials may be almost wholly dissolved and deposited at or below the level of ground water

by the reactions above stated, as at Ducktown, Tenn., or partly dissolved and transported below, as at Butte, Mont. Thus for a certain depth the ores may increase in richness. This exception, however, does not affect the common rule as to diminution of richness with increasing depth.

Penrose,[a] in 1894, in discussing the superficial alteration of ore deposits, says:

> As a result of these various changes, certain materials are sometimes leached from the upper parts of ore deposits, which have become porous by alteration, and carried down to the less pervious unaltered parts. Here they are precipitated by meeting other solutions, or in other ways, and hence the richest bodies of ore in a deposit often occur between the overlying altered part and the underlying unaltered part. This is not always the case, but it is true of some copper, silver, iron, and other deposits.[b]

De Launay,[c] in 1897, emphasizes the frequent occurrence near the surface of rich deposits, which in some cases are oxidized products and in others are sulphides. He explains the richness of the deposits by the abstraction of more soluble material. This frequently results, he thinks, in transforming a low-grade product into a rich ore. By this process a poor sulphide may be changed to a rich sulphide, as, for instance, cupriferous pyrites or chalcopyrite may be transformed to covellite or chalcocite by abstraction of iron sulphide. It is a natural deduction from de Launay's explanation[d] that the volume of the material is decreased, although he does not make this point.

De Launay further emphasized the point that the metallic material of veins may have been repeatedly transferred from one place to another, and suggests that a part of the material now found in veins may have been transferred from vein material which was once above the present surface of denudation.

Le Conte[e] suggested that the rich belt may be explained by supposing that precipitation by ascending waters does not occur at great depth, because the solutions do not get saturated until comparatively near the level of underground water. But it is to be remembered that the upper

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[a] Penrose, R. A. F., jr., The superficial alteration of ore deposits: Jour. Geol., vol. 2, 1894, pp. 288–317.

[b] Penrose, cit. p. 294.

[c] Launay, M. L. de, Contributions à l'étude des gîtes métallifères: Annales des Mines, 9th ser., vol. 12, 1897, pp. 151–152.

[d] Launay, de cit. p. 194.

[e] Le Conte, Jos., On the genesis of metalliferous veins: Am. Jour. Sci., 3d series, vol. 26, 1883, p. 12.

part of a fissure receives abundant lateral waters which have been transported a comparatively short distance under conditions of low pressure and temperature; whereas the solutions lower down have taken a longer journey under conditions of high pressure and temperature. If Le Conte's explanation be satisfactory, one would expect the most insoluble constituent to be precipitated at the greatest depth. In the case of the lead-zinc-iron deposits this would make the galena abundant at depth, the sphalerite abundant at a higher level, and the iron sulphide the dominating constituent at the highest levels. In the case of the copper-iron deposits the rich sulphides of copper would be in the lower levels and the cupriferous pyrites at the higher levels.

From the foregoing it is apparent that there has been a general understanding that a rich upper belt has been produced in many ore deposits. My explanation of a rich upper belt is, mainly, that oxidized soluble compounds are produced in the belt of weathering, and that these in situ or lower down react upon the lean sulphides and tellurides. In this way a rich belt is formed. Later, in consequence of denudation, these rich sulphides and tellurides pass into the belt of weathering. Here they are again exposed to the oxidizing forces, are largely transformed in situ to oxides, carbonates, etc., and a belt of rich oxidized products is formed above the ground water. In part, when oxidized, the materials are taken into solution, again transported downward, and again react upon the sulphides and tellurides. In arid regions, where the amount of downward-moving water is small, the oxidized products formed from the rich sulphides and tellurides are likely to remain in large part in situ; but in humid regions, where water is abundant, the metals, after oxidization, are in large measure carried downward and again react upon the sulphides and tellurides below and further broaden and enrich this belt. Thus, under different climatic conditions, we may have a rich oxidized zone, a rich sulphide and telluride zone, or both, in varying proportion.

It is notable that the vertical distribution of the sulphides in the rich zone is precisely that which should be expected from the affinity of the metals for sulphur In the lead-zinc-iron districts the galena is found at the highest horizon, lower down is the sphalerite, and still lower the iron sulphide. In the copper-iron lodes the high-grade copper sulphides, chalcocite and bornite, are at higher levels; lower these are intermixed

with chalcopyrite; still lower the chalcopyrite is mixed with pyrite; and in the deepest levels the pyrite is dominant. Apparently this vertical arrangement of the sulphides can not possibly be explained by precipitation by ascending waters. From such waters we would expect exactly the reverse distribution.

While the reaction between the oxidized products and the sulphides has been strongly emphasized, because it is believed to be the most fundamental of the causes producing a rich upper belt, it is understood that other factors may also help in this process. As already pointed out, reduction and precipitation of the metals of descending solutions may take place through the agency of organic matter or other reducing materials contained in the rocks, or by meeting ascending solutions carrying precipitating agents. Near the surface more than an average amount of original precipitates from ascending solutions is a possibility in some cases. (See p. 1077.)

Concluding, it appears to me that the existence of a rich upper belt in many deposits, and the frequent diminution of the ores in richness in passing from the surface to some distance below the level of ground water, can not be the work of ascending or descending waters alone, but is due to ascending and descending waters combined. Ascending waters produce a first concentration. A second concentration by descending waters produces the rich deposits. These rich products are found in the few meters or few hundred meters of the outer crust of the earth. When it is remembered that the greater part of the ores which have yet to be abstracted from the earth comes from the first 500 or 700 meters, and when it is further considered that the effect of descending waters may be felt to these depths, it becomes evident that the process of second concentration by descending waters is a very important one indeed, so far as the economic value of ore deposits is concerned. Indeed, as a result of it there is concentrated in the extreme outer shell of the crust of the earth a large portion of the products which during the first concentration may in many cases have been distributed over 1,500 or 3,000 meters or more, but which have now been largely removed by erosion. We therefore conclude that for a large class of ore deposits a second concentration by descending waters can not be said to be one whit less important in the genesis of ores than a first concentration by ascending waters.

It follows from the foregoing that one of the most important classes of ore deposits is that produced by the joint action of ascending and descending waters. First comes the action of the downward-moving, lateral-moving waters, mainly of meteoric origin, which take into solution metalliferous material. In regions of recent volcanism these waters may be joined by subordinate amounts of water exuded during the crystallization of magmas; and such waters may be rich in metallic material. The waters, after collecting metals from any or all of the rocks with which they come into contact, are converged into trunk channels and there, while ascending, may deposit ore of the first concentration. During and after this first concentration many of the ore deposits which are worked by man have undergone a second concentration not less important than the first as a result of descending lateral-moving waters. In some cases a concentration by descending lateral-moving waters alone is sufficient to explain ore deposits. It, therefore, appears more clearly than heretofore that an adequate view of ore deposits must not be a descending-water theory, a lateral secreting water theory, or an ascending-water theory alone. The descending, lateral-moving, and ascending waters alike are driven mainly by gravity. Each performs its own work.

SUBCLASS 3. ORES PRECIPITATED FROM DESCENDING AQUEOUS SOLUTIONS.

For the sake of simplicity and continuity of exposition, the effects produced by descending waters have been applied to deposits which have been first concentrated by ascending waters. However, it is perfectly clear that a concentration by descending waters alone may be adequate to produce ore deposits. The more important ores which are produced by descending waters alone are those of iron and manganese. The ores of these metals thus formed are chiefly oxides, and so far as iron and manganese are concerned are largely hydrated oxides.

IRON ORES.

The ores of iron, unlike those of the other metals, occur in such large masses that they properly belong with the rocks, hence their general development has been already considerered in Chapters IX and XI. It remains here only to summarize the special factors which have been of consequence in their segregation. Of the ore deposits which it has been

shown are produced by descending waters alone, those of the Lake Superior region are unquestionably of the greatest importance.

In another place I have fully discussed the segregation of these iron-ore deposits.[a] Without exception the great iron-ore deposits of the Lake Superior region are found resting upon impervious formations. In the great majority of cases these impervious formations are in pitching troughs. (See Pl. XIII.) Thus the trunk channels of circulation are formed. For the most part these troughs are somewhat close and have steep pitches, but in the Mesabi district the troughs are less definite in form and have a very shallow pitch. The impervious basement for an iron ore deposit may be an impervious sediment such as a slate, may be an igneous rock, or a combination of the two. The essential thing is that the basement shall be relatively impervious to water as compared with the iron-bearing formation in which the ores occur. The source from which the iron oxide is obtained is the original rock of the iron-bearing formation, either siderite or hydrous ferrous silicate, greenalite. As the water starts on its downward journey the oxygen it contains is exhausted in the oxidation of the iron carbonate or ferrous silicate, thus producing the ferruginous slates and cherts, at the same time liberating the carbon dioxide of the carbonates. The waters from which the oxygen is exhausted and which are enriched in carbon dioxide are now able to take the ferrous carbonate and hydrated ferrous silicate into solution. Where impervious basements exist in pitching troughs, the downward-moving waters are deflected toward these, and thus are converged into such troughs. Other waters more directly from the surface which have not come into contact with iron carbonate and iron silicate, and therefore bear oxygen, are also converged into the troughs. The mingling of the two classes of waters in the troughs results in the precipitation of the hydrated hematite and limonite, the reaction in the case of the iron carbonate being:

$$2FeCO_3+nH_2O+O=Fe_2O_3.\,nH_2O+2CO_2$$

At the same time the abundant waters converged in the trunk channels dissolve the silica, and thus the ores are depleted in that compound. So far as there was iron carbonate or iron silicate in the pitching troughs the ferrous oxide is largely oxidized in situ. Thus, the ore deposits are the

[a] Van Hise, C. R., The iron-ore deposits of the Lake Superior region: Twenty-first Ann. Rept. U. S. Geol. Survey, pt. 3, 1901, pp. 305–434.

PLATE XIII.

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PLATE XIII.

IRON ORE DEPOSITS IN PITCHING TROUGHS.

(Both ore exploited and ore now in mine are represented as ore, since the purpose of this plate is to show the manner of the development of the ore rather than the present stage of exploitation.)

Fig. 1. Vertical north-south cross section of Chandler mine, showing relations of the ore deposit to the soap rock, Ely greenstone, and ore-bearing formation. The iron ore is in a broad U-shaped trough, bottomed by soapstone or paint rock which grades down into greenstone. It is capped by the ore-formation material. At the place where the cross section is made the ore does not extend to the surface along either limb. Therefore, at the particular place where this cross section exists, although there is a very large ore deposit below the surface, at the surface the only rocks which are found are the greenstone, soapstone and iron-bearing formation.

Scale: 1 inch equals 250 feet.

Fig. 2. Vertical east-west longitudinal section of Chandler mine, showing the same relations as fig. 1. The figure very well illustrates how the ore body increases in size from the surface. Where the ore reaches the drift its area is small; and this great ore deposit, which extends eastward, where it constitutes the Pioneer mine, is below a heavy capping of the ore-bearing formation.

Scale: 1 inch equals 250 feet.

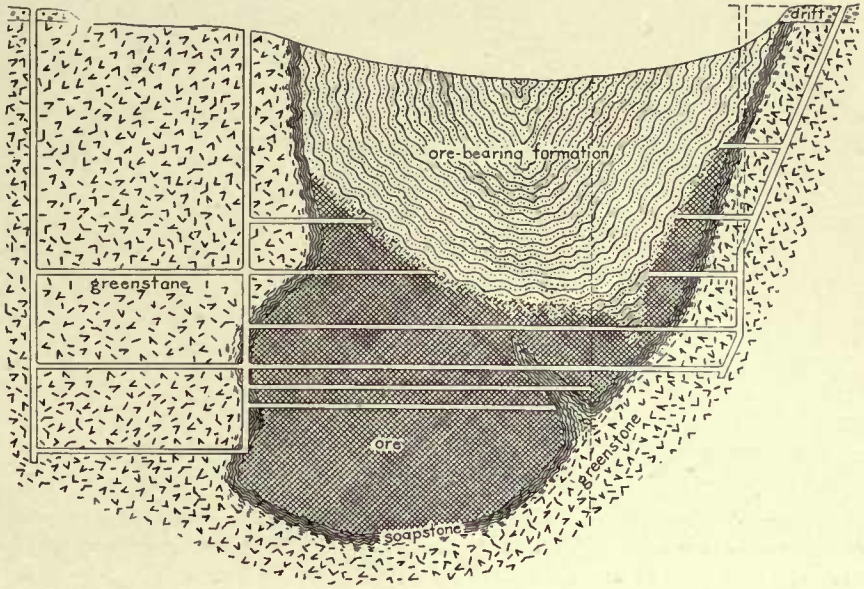

Fig 1

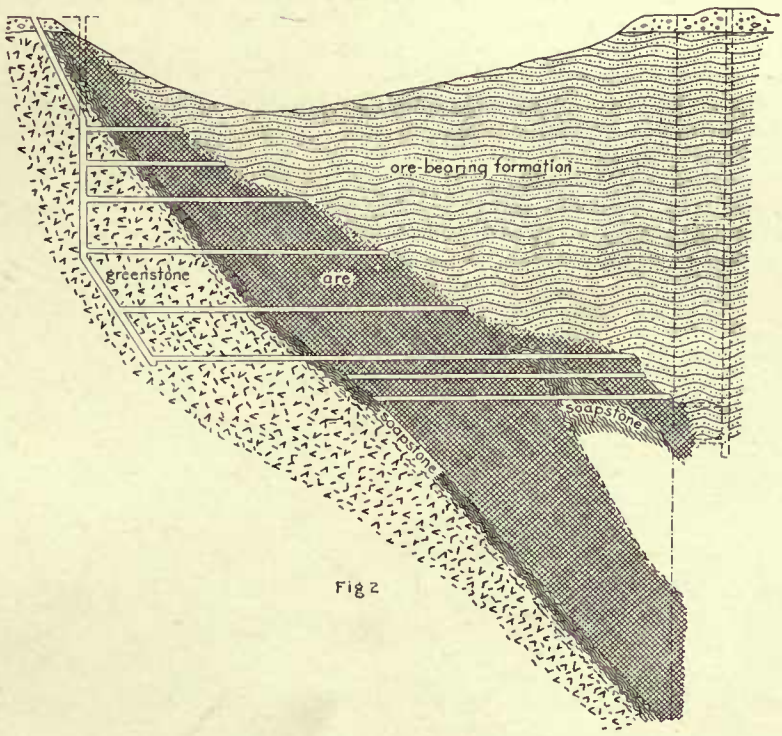

Fig 2

IRON-ORE DEPOSITS IN PITCHING TROUGHS.

result largely of the transportation of iron carbonate to the pitching troughs, the iron being there precipitated, and partly of oxidation of ferrous carbonate or silicate in place. Simultaneously with these processes the silica is dissolved and abstracted.

It is to be noted that the precipitation of iron ores by the above process is due essentially to the mingling of solutions from two different sources. The solutions from one source have taken a longer journey, or else have passed through rocks more capable of abstracting oxygen, so that they early acquired the properties of deep solutions—an excess of carbonic acid and an absence of oxygen. Under such circumstances they carry iron carbonate precisely as do the deep solutions of the first concentration in ores produced by ascending waters. The solutions from the other source pass through material in which the iron has already been oxidized to the ferric form, and therefore do not have the oxygen extracted. The course of this water is not necessarily shorter than that of the other waters, but upon the average is likely to be so. When the two solutions come together the iron oxide is precipitated, in consequence of the mingling of solutions. While for the Lake Superior iron ores apparently the solutions from both sources were descending to the point where they became mingled, in iron-ore deposits in other regions it may be found that the precipitation of the iron oxide was due to the mingling of ascending solutions bearing iron carbonate with descending solutions bearing oxygen.

For instance, at certain localities the iron ores are magnetite instead of hydrated hematite. In Chapter IX the various ways in which magnetite may be produced are discussed, but it may be suggested that magnetites may be due to the direct precipitation of ascending solutions bearing iron carbonate and descending solutions bearing an insufficient amount of oxygen for transformation to the ferric oxide, the reaction being as follows:

$$3FeCO_3+O=Fe_3O_4+3CO_2.$$

Perhaps the most notable magnetite deposit in the United States is that of the Cornwall mine in Pennsylvania. Here the ore is a replacement of Silurian limestone, and rests upon a trap dike as an impervious basement. The Mesozoic rocks are faulted against the limestone and ore. A plausible suggestion as to the origin of this deposit is that ascending waters bearing iron carbonate, moving up along the fault and through the limestone, met

descending waters bearing oxygen and following the impervious basement, and as the oxygen was not in sufficient quantity to oxidize the iron to the ferric oxide it was thrown down as magnetite.

It has been pointed out (pp. 845–846), that magnetite may be produced in two other ways—by the reaction of siderite and pyrite upon each other, or by the partial oxidation of pyrite or pyrrhotite. In the Cornwall deposits[a] sulphur is a constant associate in small percentage except at the surface, and this fact suggests the possibility that the reactions between iron carbonate and iron sulphide or between iron sulphide and oxygen may have been also instrumental in the production of the magnetite; but the amount of residual sulphur is so small that the theory of the derivation of the deposit in large measure from pyrite has scanty support.

To what extent the principles worked out in reference to the Lake Superior ores are applicable to the iron-ore deposits of other parts of the world it is yet too early to say, but, as just suggested, the descriptions of the Cornwall deposit show that it has many features in common with the ores of the Lake Superior region. Many of the Silurian deposits of the Appalachian region are at contacts of limestones with shale or slate. In some places these latter are certainly in such positions as to furnish impervious basements, and therefore the ores present many features analogous to those of the Lake Superior region. But a much more extended study of the iron-ore deposits of other regions must be made before any generalization can be made with reference to them.

MANGANESE ORES.

The manganese deposits, like the iron-ore deposits, are very largely secondary segregations by descending waters. Indeed, iron and manganese are very closely associated. Many of the iron-ore deposits are manganiferous, and some of them sufficiently so locally that they also become ores of manganese. For instance, in the Gogebic district of Michigan a small amount of the iron ore was sufficiently manganiferous to be sold as a manganese ore rather than an iron ore. Manganese ores are always associated with iron oxide. The amount of iron is variable, running from a small percentage to an amount considerably in excess of the manganese.

[a] Lesley, J. P., and d'Invilliers, E. V., Report on the Cornwall iron-ore mines, Lebanon County: Ann. Rept. Geol. Survey Pennsylvania for 1885, pp. 533–534.

Manganese is present in the original igneous rocks in very much smaller quantity than iron, and therefore the manganese deposits are much smaller than those of iron; but so far as can be made out, the segregation of manganese and iron are strictly parallel processes. Thus in the secondary rocks manganese is found only as traces in the sandstones and shales, but in the limestones—carbonate rocks—it is more than half as abundant as in the original rocks. Since the limestones are so small in mass, only a small fraction of the manganese of the original rocks is in the limestones. Apparently the great mass of the manganese of the original rocks has been segregated in the ores of manganese and iron and in the iron formations.

In view of all the foregoing facts it is thought to be extremely probable that the manganese is largely transported as a carbonate from the original rocks to lagoons, and is there precipitated as an oxide. By this process bog ores of manganese are produced just as are the bog limonites. But to a large extent the manganese oxide is reduced to the manganous form by the organic matter, reunites with carbon dioxide, forming carbonate, and in this form is built up into carbonate formations. From such carbonate formations it is segregated by underground solutions which have different sources and mingle in the trunk channels. Some solutions bear the manganese carbonate and others the oxygen. When these two meet the manganese is precipitated as hydrated oxide according to the following reaction:

$$MnCO_3 + O + nH_2O = MnO_2 . nH_2O + CO_2.$$

It is yet too early to state to what extent the manganese ores have been concentrated on impervious basements in pitching troughs.

IV. SPECIAL FACTORS AFFECTING THE CONCENTRATION OF ORES.

Thus far the discussion of ores deposited from aqueous solutions has not taken into account a number of the special factors which affect the concentration of ores. The general discussion may need great modification to adapt it to a particular district. To illustrate my meaning, it may be well to consider some of the additional factors affecting the deposition of ores, and to point out the more obvious possible modifications of the general theory which may result from them. There will be briefly considered the effect of (1) variations in porosity and structure, (2) the character of the topography, and (3) physical revolutions.

VARIATIONS IN POROSITY AND STRUCTURE.

It has been fully explained that a vigorous circulation is essential for the production of aqueous ore deposits. It has been pointed out that in order to produce an ore deposit the amount of water which must flow through the openings is many thousands of times the volume of the ores deposited. Also it has been explained that waters do not produce channels. In order to have a vigorous circulation original and continuous channels must exist. Thus initial porosity in rocks is an essential factor in the development of ore deposits. In the foregoing discussion the existence of trunk channels has been recognized, but otherwise it has been assumed that the rocks were equally porous in all directions. As a matter of fact, the rocks range between the widest extremes in porosity; from those in which the openings are subcapillary and which are substantially impervious to those which are as open as a sieve in all directions.

The different masses of sedimentary rocks, igneous rocks (especially the lavas), and metamorphosed equivalents of either sedimentary or igneous rocks may differ in porosity.[a] The contacts of rocks of different kinds frequently furnish trunk channels for circulating water. Bedding partings produced by shearing stresses during deformation furnish sheet channels parallel to the strata, or openings on the anticlines or synclines. Some strata when deformed may yield by fracture, furnishing channels for water circulation, while interlaminated strata may yield by flowage, thus remaining relatively impervious. These various irregularities may combine in different ways.

All irregularities in porosity and structure require modification of the simple general statements of the present paper (see pp. 129–156, 571–589) concerning the character of underground circulation and the concentration of ore deposits. At some time it may be possible to divide the modifications of the general circulation due to variation of porosity and structure into classes, but at present this can not be done. The modifications of the general circulation which occur in many districts must first be studied and described individually, after which generalizations may possibly be made. At present some statements may be made in reference to certain modifications of the underground circulation.

[a] Compare Emmons, Structural relations of ore deposits: Trans. Am. Inst. Min. Eng., vol. 16, 1888, pp. 804–839.

DISTRIBUTION AND SIZE OF OPENINGS.

From the foregoing general statement it is clear that one of the essential conditions for the production of large ore deposits is that openings should be of adequate size. As will be seen, these openings may be original or they may be largely secondary. A close analysis of the manner in which the waters work shows that it is not of advantage in ore deposition to have equal porosity in all directions. Were the rocks equally porous in every direction there would be no reason for the concentration of the water in trunk channels, and therefore the conditions which have been discussed as essential for the mingling of solutions of different kinds would not exist. Oftentimes the essential condition is to have considerable masses of rocks nonporous or moderately porous adjacent to or associated with other areas which are very porous. Oftentimes where the porous belts are too numerous there is a segregation of a small amount of ore in them all, and not an adequate segregation in any one.

The most frequent combination of porous and relatively nonporous rocks favorable to the production of ore deposits is to have certain belts with openings of adequate size associated with more extensive areas in which the openings are much smaller, although they may be equally continuous. As illustrations of such combinations we may have layers of sandstone or conglomerate between igneous rocks or shale. The large openings may be furnished by fault fissures.

For many reasons trunk channels may vary greatly in size and continuity. For instance, fault fissures, in consequence of the irregularity of the fractures and the displacements, may range in width from great rooms to mere seams. The effect of the dip upon fissures is of great importance. Where the dips are vertical or nearly so, the veins may be wide; whereas, where the dips are flat, the veins may be relatively narrow. This is a natural consequence of the effect of gravity. The more inclined the veins the more forcibly does gravity pull down the overhanging wall, and thus tend to close the openings. This association of wide veins with steep dips, and narrow veins with low dips, is beautifully illustrated at the Smuggler Union mine, of southwestern Colorado.

COMPLEXITY OF OPENINGS.

In the general discussion an ore deposit has been spoken of as if it were a single continuous mass formed in a large opening. An ore deposit in a single large opening is exceptional. Ore deposits show all gradations of openings from large single ones to those of an extraordinarily complex character. A trunk channel may be a set of distributive faults; a group of parallel or intersecting sets of joint openings; the minute parallel openings of fissility; a group of openings along bedding planes; the shrinkage openings formed within or along the borders of cooling magma; the openings in an autoclastic rock or reibungs breccia; the multitude of openings of a sandstone or a conglomerate; or the very minute openings between the mineral particles of a limestone, schist, gneiss, or other dense rocks.

Trunk channels may vary from vertical to nearly horizontal attitudes. Ore deposits ordinarily have important vertical components, although they may be found in nearly horizontal positions. In the latter case the trunk channels forming the deposits probably have vertical components somewhere else.

It is hardly necessary to give illustrations of ore deposits for each of these complex conditions, but, as very excellent instances of veins of a very composite character may be mentioned the Cripple Creek deposits[a] and the gold-quartz veins of Nevada City and Grass Valley, Cal.[b] The essential point, so far as the discussion of the foregoing pages is concerned, is that ore deposits commonly occur at places where there are trunk channels for ascending or descending waters, or both. In order that metalliferous material shall be brought to a place and deposited in large quantity, there must be long-continued circulation. It matters not whether a trunk channel is a single passage or is composed of an indefinite number of minor passages, the principles given on the previous pages are applicable to the deposition of ores in such trunk channels.

In various regions the conditions are so exceedingly complex that ore deposits close together may differ greatly in their mineral content. This is the best evidence that, notwithstanding their continuity, the under-

[a] Penrose, R. A. F., jr., Mining geology of the Cripple Creek district, Colo.: Sixteenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1895, pp. 137–153.

[b] Lindgren, Waldemar, The gold-quartz veins of Nevada City and Grass Valley, California: Seventeenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1896, pp. 158–160, 259.

ground systems of water circulation have been, if not independent, at least partly so. This is well illustrated by the ore deposits of Butte, Mont. Apparently the metallic contents of the individual feeding streams and even the trunk channels were very different within short distances. There are two main zones of mineralization. The more important product of one of these mineral zones is silver sulphide, which is associated with sulphides of lead, zinc, and iron, and with silicate of manganese. The chief product of the other mineral zone is copper, which carries silver in important amounts.[a]

PREEXISTING CHANNELS AND REPLACEMENTS.

When it is understood that ore deposits from aqueous solutions ordinarily form in trunk channels the question as to whether ores are deposited in preexisting openings or are replacements is easily answered, as a general proposition. It has been shown that such channels are not originally formed by aqueous solutions. (See pp. 1007–1008.) Original channels for underground circulation are primarily due to the structures of rocks or to the effects of deformation. It therefore follows that ores are, to some extent at least, deposited in preexisting openings. However, the conditions favoring vigorous circulation are also those causing reactions on the wall rocks. It has been fully explained that solution and deposition are commonly simultaneous processes. Wherever there is a trunk channel it is certain that the walls of the openings are dissolved to some extent, and at the same time, or subsequently, metalliferous minerals are precipitated. Indeed, either enlargement by solution and subsequent precipitation of ore, or synchronous solution and precipitation by which the wall rocks are replaced in various degrees, molecule by molecule, by the ore, or both together, are almost universal phenomena.

I therefore believe that the large majority of ore deposits, if not all, are partly deposited in preexisting openings and are partly replacements of the wall rocks. However, in some cases the filling of the preexisting cavities is more important, and in other cases substitution for the wall rocks is the dominant process.

Other things being equal, ore deposits which are largely in preexisting cavities are more likely to occur in strong refractory rocks, such as quartzite,

[a] Emmons, S. F., Notes on the geology of Butte, Montana: Trans. Am. Inst. Min. Eng., vol. 16, 1888, p. 54.

granite, and porphyry; and ore deposits which are largely replacements are more likely to be found in easily soluble rocks, such as limestone. The gold-quartz veins of California give an excellent illustration of the deposition of ores in preexisting cavities in refractory rocks, such as siliceous argillite, diabase, diorite, and granodiorite.[a] This case is all the more interesting since the wall rock itself is greatly modified, and has lost and gained various elements. The San Juan district of southwestern Colorado furnishes another excellent illustration of veins deposited in openings of hard, refractory rocks. Here great continuous lodes in preexisting openings are known to extend for a vertical distance of 1,000 meters or more; but even here there is very frequently complex fracturing or even brecciation, as a result of which the veins form either a series of sheets separated by layers of wall rock or breccia cemented by vein material. Ore deposits which are largely replacements in easily soluble rocks are well illustrated by the silver-lead deposits of Eureka, Nev.,[b] and Leadville[c] and Aspen,[d] Colo.

Replacements are likely to be important also in proportion as the trunk channels are complex rather than simple. This follows from the law of mass action. In proportion as a trunk channel is complex, the surface of action upon the wall rock for a given quantity of solution is large. As conspicuous examples where there are large surfaces of action may be mentioned sandstones and conglomerates and the reibungs breccias, or crushed rocks along fault zones. Where the trunk channels are very complex, the rocks, even if refractory, may be replaced to a considerable extent by the metalliferous ores. A conspicuous instance of this in a sedimentary rock is that of the copper conglomerate deposits of Lake Superior, where many grains, pebbles, and bowlders of porphyry are partly or wholly replaced by metallic copper. On some bowlders the metallic copper occurs as partial or complete skulls surrounding the fragments of porphyry; in others these skulls are thicker, and in still others the entire masses of the bowlders, as described by Pumpelly,[e] are fully replaced by

[a] Lindgren, cit., pp. 172–257, 259, 261; also pp. 146–157.

[b] Curtis, J. S., Silver-lead deposits of Eureka, Nev.: Mon. U. S. Geol. Survey, vol. 7, 1884, pp. 93–106.

[c] Emmons, S. F., Geology and mining industry of Leadville: Mon. U. S. Geol. Survey, vol. 12, 1886, pp. 565–569.

[d] Spurr, J. E., Geology of the Aspen mining district, Colorado: Mon. U. S. Geol. Survey, vol. 31, 1898, pp. 231–234.

[e] Pumpelly, R., Copper district: Geol. of Michigan, vol. 1, pt. 2, 1873, pp. 37–38. Pumpelly, R., The paragenesis and derivation of copper and its associates on Lake Superior: Am. Jour. Sci., 3d series, vol. 2, 1871, pp. 348–355.

the metallic copper. While the conglomerate deposits of Lake Superior are in part replacements, they also are in large part fillings of preexisting cavities between the clastic particles. An excellent example of replacement in igneous rocks where there is wonderfully complex distributive faulting and folding, and thus a large surface of contact for substitution, is furnished by the Cripple Creek district, in which, according to Penrose,[a] ore mainly occurs replacing and blending into various igneous rocks.

By substitution a rock may be completely replaced by ore. This is particularly likely to occur where the rock is uniform in structure and composition, as limestone or dolomite. Where, on the contrary, the rock is of complex composition, such as granite or porphyry, or where there are different kinds of rock present, as, for instance, diorite and granite, the replacement is usually largely selective. This selective replacement may apply to the mass of the wall rock, to the individual fragments of it, to clastic fragments of sandstones or conglomerate, and to the different constituent minerals in a single fragment. The particular minerals or masses which are most soluble in the solutions present are most rapidly dissolved. Where the wall rock varies greatly in the solubility of its minerals the selective replacement of the country rock may extend for some distance from the central deposits. The readily soluble minerals are dissolved, and in place of them are precipitated the metalliferous minerals. This process is ordinarily called impregnation. Selective replacement of this kind is well illustrated by the Butte, Mont., granite, in which "the basic constituents of the granite are naturally attacked first, then the feldspars, and finally the quartz itself may be removed, so that in some parts there are found large masses composed entirely of metallic minerals."[b]

In regions of heterogeneous rocks the frequent occurrence of main masses of the ore deposits in the more soluble rocks is due in part to its greater solubility. For instance, where limestone occurs in intimate association with sandstone, with quartzite, with diorite, with trachyte, with porphyry, with granite, or with almost any other rock, and ore deposits are found, the ore is likely to be largely in the limestone, partly because it is

[a] Penrose, R. A. F., jr., The mining geology of Cripple Creek, Colorado: Sixteenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1895, pp. 140–141, 144–146, 161–162.

[b] Emmons, S. F., Notes on the geology of Butte, Montana: Trans. Am. Inst. Min. Eng., vol. 16, 1888, p. 57.

more soluble than the other rocks.[a] But other factors enter into the matter. It has already been explained that country rock, especially limestone, may furnish solutions which react on the mineral-bearing solutions and thus cause precipitation or furnish the metallic material. (See pp. 1086–1087.) Furthermore, where limestone and stronger rocks are deformed together, the limestone, having less strength, is more likely to be crushed and broken in a complex manner and thus furnish trunk channels for circulation.

Change in the level of ground water may be an important factor in opening up rooms in which ores may be deposited later. It is explained (pp. 409–411, 565–566) that for various reasons the level of ground water may vary greatly, and that above it large openings, such as caves, are formed. (See pp. 484–487.) If, later, the level of ground water for any reason rises, these openings pass into the belt of cementation and in them large ore bodies, including sulphides, may be deposited. This may be the history of the great cave-like openings, lined with gigantic geodal crystals, which are found in the lead and zinc districts of Missouri, and which were below the level of ground water before pumping was begun. While the larger caves apparently have not been especially favorable places for ore deposition, in some of the smaller ones ores have been deposited. Probably this history applies to the Butte district. Emmons[b] says that for this district the level of ground water was once very much lower than now, possibly as much as 300 to 600 meters. Doubtless much of the solution occurred when the water was at a lower level. Later, when the ground-water level was raised, the openings formed by solution were utilized by the ore precipitated from descending waters transporting material from higher levels. This process may have been important in the development of the large sulphide bodies now below the level of ground water.

In conclusion, I hold that ores deposited from aqueous solutions form where there existed original trunk channels of circulation. Ore deposits

[a] Wendt, Arthur F., The copper ores of the Southwest: Trans. Am. Inst. Min. Eng., vol. 15, 1887, pp. 25–77. Curtis, J. S., Silver-lead deposits of Eureka, Nevada: Mon. U. S. Geol. Survey, vol. 7, 1884, pp. 64–79. Emmons, S. F., Geology and mining industry of Leadville: Mon. U. S. Geol. Survey, vol. 12, p. 540–543.

[b] Emmons, S. F., The secondary enrichment of ore deposits: Genesis of ore deposits, Am. Inst. Min. Eng., 2d ed., 1902, pp. 444–445. See also Weed, W. H., The enrichment of gold and silver veins: loc. cit., p. 497.

formed along trunk channels occur commonly, if not universally, to some extent in preexisting openings and to some extent as a substitution for the wall rock. Where the trunk channels are simple and the rocks refractory, the ore deposits may be largely in preexisting openings. Where the trunk channels are complex and the rocks soluble, the ore deposits to a large extent are likely to be replacements.

IMPERVIOUS STRATA AT VARIOUS DEPTHS.

Slichter's theoretical investigations on the motions of ground waters show that, in order to discuss the flowage under any given set of conditions, it must be assumed that it is limited only by an impervious stratum.[a]

It is, of course, understood that there are no strata which are absolutely impervious, but there are many which are practically so. Wherever there is an impervious stratum the effective underground circulation is there limited or divided, whether the stratum be at the depth of 100 or 1,000 or more meters. The impervious stratum may be a plastic shale which yields to deformation without fracture, or it may be a rock intruded after deformation has occurred, thus making a barrier. Of course there are all gradations, from practically impervious strata to strata which merely check the circulation. It is believed that in the average case the limit of effective circulation is probably much less than the theoretical limit of 10,000 meters given by the depth of the zone of fracture.

If an impervious stratum be but 100 meters from the surface and fissures be limited to that depth or interrupted, the laws given (pp. 1021–1028) apply to the circulation above the stratum. Therefore, such a fissure may be occupied by ascending water in the lower part and by descending water in its upper part. Hence an ore deposit contained in such a shallow fissure may be the result of a single concentration by ascending or descending waters, or of two concentrations, the first by ascending and the second by descending waters.

The foregoing statement in reference to the practical limits of underground circulation for the ore deposits of a given district may be true even if below the impervious stratum there are other strata, fed from a distance, in which circulation is occurring. Such lower pervious strata may have

[a] Slichter, C. S., Theoretical investigation of the motion of ground waters: Nineteenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1899, 329–357.

circulations of their own, independent of the higher circulations, and this circulation may produce ore bodies. This is beautifully illustrated by the Enterprise mine, of Rico, Colorado (see fig. 29), described by Rickard[a] and Ransome,[b] in which the ore is confined to fissured and broken limestones, gypsum, and sandstone below a black shale, which, when bent, did not fracture, and therefore afforded no channels for water circulation.

In this connection it may be well to mention the Mercur district of Utah (see pp. 1213–1214), where a silver ledge and a gold ledge, about 30 meters apart, occur in limestone, each below a shale-like stratum of altered porphyry. Spurr regards the silver ledge as produced during an earlier mineralizing period, and the gold ledge during a later one.[c] It may be suggested that the true explanation of the existence of two mineral ledges so near together and of such different mineral character is that in this district there were two independent circulations separated by impervious strata—the upper one, producing the gold ledge, lying between the two impervious porphyry belts; while the lower one, forming the silver deposit, was below the lower impervious layer.

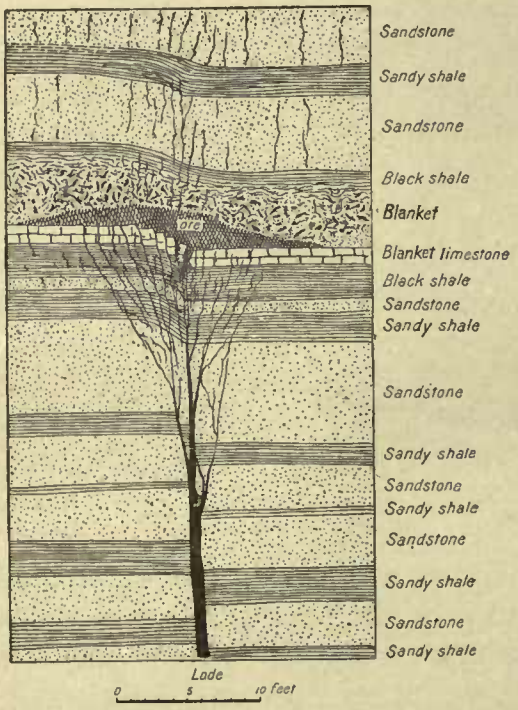

FIG. 29.—Diagrammatic section of Enterprise mine, Colorado, and its blanket pay shoot. After Ransome.

The lead and zinc ores of the Mississippi Valley[d] furnish another illus-

[a] Rickard, T. A., The Enterprise mine, Rico, Colo.: Trans. Am. Inst. Min. Eng., vol. 26, 1897, pp. 918, 960–973, 976–977.

[b] Ransome, F. L., The ore deposits of the Rico Mountains, Colorado: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, pp. 299–397.

[c] Spurr, J. E., Economic geology of the Mercur mining district, Utah: Sixteenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1895, pp. 367–369.

[d] Bain, H. F., with C. R. Van Hise and G. I. Adams, Preliminary report on the lead and zinc deposits of the Ozark region: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, pp. 33–227. Van Hise, C. R., Some principles controlling the deposition of ores: Trans. Am. Inst. Min. Eng., vol. 30, 1900, pp. 102–109. Van Hise, C. R., and Bain, H. F., The lead and zinc deposits of the Mississippi Valley: Trans. Federated Inst. Min. Eng., England, 1902, pp. 1–60.

tration in which impervious layers are of the greatest importance. Taking this region as a whole, and considering only the lithology, we have the following succession in descending order: (1) Thick shale formation; (2) limestone, bearing ore bodies; (3) shale; (4) limestone, bearing ore bodies; (5) shale, often interstratified with limestone; (6) sandstone; and (7) pre-Cambrian. As illustrating the influence of the impervious strata in the formation of the ores, we can consider more particularly two districts, the Missouri-Kansas district and the upper Mississippi Valley district.

In the Missouri-Kansas district the descending succession of strata is: (1) Undifferentiated Carboniferous sandstones and shales; (2) Lower Carboniferous (Mississippian) limestones; (3) Devono-Carboniferous shales; (4) Cambro-Silurian limestones; (5) Cambrian sandstones; (6) pre-Cambrian. In this area there was an artesian circulation in the Cambro-Silurian limestones and sandstones under the Devono-Carboniferous shales, and in the Lower Carboniferous limestones under the Carboniferous

FIG. 30.—Illustrating mingling of circulations of two limestones separated by a shale.

sandstones and shales. (See fig. 30.) Probably the deposition of the ores began in consequence of a connection of the circulations of the Cambro-Silurian and the Carboniferous limestones by faults cutting the impervious Devono-Carboniferous shales. The ores of the district are deposited in the Carboniferous limestone, which is not dolomitic. The Cambro-Silurian limestone is strongly dolomitic. A very important gangue mineral deposited with the ores in the Carboniferous is dolomite. It is therefore believed that the metals for the ores and the dolomite alike were derived from the Cambro-Silurian limestone and were precipitated in the Lower Carboniferous limestone in consequence of the reducing action of the solutions furnished by it and by the direct action of the organic matter in the shales and limestones. At an early stage of erosion, when the Carboniferous shales and sandstones were removed, the artesian water under pressure arose along joints, faults, and other trunk channels to the surface, and thus the first concentration of the sulphides in the Carboniferous limestone took

place. In some places in the district where the capping shale still remains, apparently little or no secondary concentration has taken place; but at many places the capping shale has been largely removed, and in such areas descending waters have produced the oxidized ores above the level of ground water, have enriched the sulphides below it, and have formed the vertical arrangement of the lead and zinc ores described on pages 1144–1145.

In the upper Mississippi Valley district it is believed that the lead and zinc have undergone two concentrations, as in the Missouri-Kansas district, although the evidence is not quite conclusive. Here Galena limestone is overlain by the Cincinnati shale, in Iowa called the Maquoketa shale,

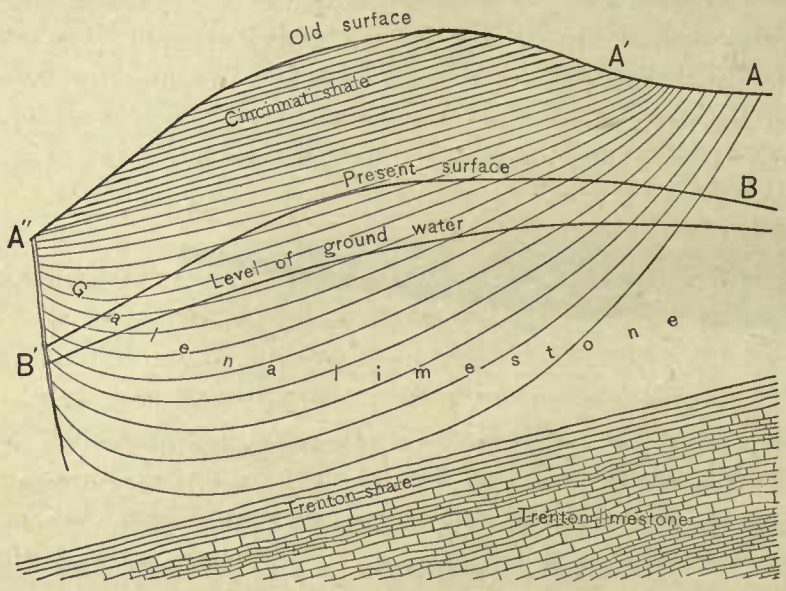

FIG. 31.—Idcal vertical section of flow of undergrounnd water in the Galena limestone of the upper Mississippi Valley. When the surface was at A A′ A″ the first concentration by ascending water took place; when erosion had redneed the surface to B B′ the second concentration hy descending water occurred.

and is underlain by the Trenton limestone, with an oil-bearing shale between. When the impervious overlying shale was partly removed an artesian circulation was inaugurated which resulted in the first concentration. Later, when the overlying shale was largely removed, a second concentration by descending waters took place, which has continued to the present time. (See fig. 31.)

The main difference between the upper Mississippi Valley and Missouri-Kansas districts is that in the upper Mississippi Valley district the important metals are believed to have their chief source in the limestones in which

the deposits are now found; whereas, as has been pointed out, in the Missouri-Kansas district the source of the ore is believed to be the Silurian dolomite and the deposits are in the overlying Carboniferous limestone. The lead and zinc deposits of central and southeastern Missouri are more nearly analogous in their history to the Upper Mississippi Valley district than to the Missouri-Kansas district.

PITCHING TROUGHS AND ARCHES.

Another interesting special case of influence of porosity and structure is that where alternately pervious and impervious layers are in a set of pitching folds. The varying porosity may follow from original difference in the porosity of the layers, or it may result from the deformation itself. The more rigid strata may be deformed by fracture, and the less rigid by flowage. The convex sides of the brittle layers are likely to be more fractured, and therefore more porous than the concave sides. For synclines this would place the more porous parts of a stratum at the bottom and for anticlines at the top.

Where strata are deformed so as to produce a set of similar or nearly similar folds, if no openings are produced at the synclines and anticlines, the layers on the limbs of the folds must be thinned and those on the arches and troughs thickened, or both. But more frequently, in the zone of fracture, instead of the layers on the limbs being thinned and the arches and troughs thickened sufficiently to occupy all the space, openings form on the anticlines and synclines, thus furnishing trunk channels. Where the folds are large, on account of their being less weight above an arch than above the corresponding syncline, the openings of the anticlines tend to be larger; but this does not apply to anticlines and synclines which are at the same level.

Any combination of porous layers with impervious layers in folds is likely to give trunk channels for underground water in the troughs above impervious strata, and at the crests below impervious strata. When descending waters come into contact with an impervious stratum, they are deflected toward the synclines, and there finding trunk channels, they follow the troughs downward along the pitch. When ascending waters come into contact with an impervious stratum they are deflected toward the anticlines, and there finding trunk channels they follow the arches upward along the pitch. Therefore, ore deposits produced by descending waters are often

found in pitching troughs underlain by relatively impervious strata; and ore deposits produced by ascending waters are often found in pitching arches overlain by impervious strata.

If this statement be reversed we have the suggestion that where ore deposits occur in connection with pitching anticlines and synclines, their positions furnish a criterion by which it may be decided whether their first concentration was accomplished by ascending or descending waters. Where the ores occur in pitching arches bounded above by impervious strata, the presumption is that they were concentrated by ascending waters; where the ore deposits occur in pitching troughs bottomed by impervious strata, the inference is that they were concentrated by descending waters, for it is difficult to see how waters can be converged at such positions by moving in the reverse directions. Of course this criterion can not be too rigidly applied, for independently of the impervious strata, openings which so frequently occur on anticlines and synclines might furnish trunk channels which could be taken advantage of by ascending or descending waters.

The Lake Superior iron ores furnish an admirable illustration of the concentration of ores by descending waters in pitching troughs which are on impervious basements. Since these ore deposits, which fully illustrate the principles of concentration of ores by descending water in pitching impervious troughs, have already been discussed, ores of this class will not be here further considered. (See Pl. XIII.)

A case in which ore is probably deposited by ascending waters in arches, because there concentrated by impervious roofs, is furnished by the Bendigo gold district of Australia.[a] The typical position for the gold in the district, according to Rickard, is immediately below a slate, on top of a sandstone. The slate is the impervious stratum and the sandstone the pervious stratum. In this district there are a large number of alternations of pervious and impervious strata, as a result of which concentrations have occurred at a number of horizons, one above the other. While Rickard does not specifically speak of the pitch of the anticlines, the longitudinal sections show that they do have a marked pitch.

It is not supposed that the location of ore deposits in pitching arches below impervious strata is wholly controlled by the existence of the impervious roofs, for, as already explained, when a heterogeneous mass of strata is

[a] Rickard, T. A., The Bendigo gold field: Trans. Am. Inst. Min. Eng., vol. 20, 1892, pp. 463–545.

folded, openings are likely to be formed at the anticlines and synclines. Rickard's explanation of the location of the ores is that the apices of the anticlines furnish more open passages than the synclines. As already explained, if it be assumed that there be less load above the anticlines than above the synclines, this would be favorable to the production of larger openings at the anticlines. This explanation may possibly be to some extent applicable, but the pitching arches concentrating the ascending solutions below impervious strata are believed to be an important factor in the localization of the ores. Various other factors—for instance, intersecting fractures—may be very important in the process. The Bendigo gold fields are very interesting in a scientific way in that such a large number of bonanzas have been found at a depth of 600 to 700 meters.[a] At the present time information is not available which adequately explains these bonanzas.

A pervious layer or other opening furnishing a trunk channel for circulating waters may be bounded on both sides by impervious strata. An excellent illustration of ore deposits at the openings of anticlines between relatively impervious strata, presumably formed by ascending waters, are the gold-bearing quartz ores in the slates and quartzites of Nova Scotia, described by Faribault.[b] Here are a great many parallel deposits directly at the anticlines or on some parts of the anticlinal folds, the deposits being separated by layers of relatively impervious slate. Furthermore, the largest deposits are located on the great pitching anticlines rather than on the subordinate ones.

Another excellent illustration of ascending ore solutions concentrated by an impervious roof is furnished by the Mercur district, Utah, described by Spurr,[c] where two ore-bearing beds, one called the silver ledge and the other the gold ledge, about 30 meters apart, occur in a limestone below seams or beds of very much altered porphyry resembling shale. The ores are especially localized where fissures reach these beds, and thus displace them, and in some cases form local arches. Moreover, the entire ore district is located upon a general anticline, furnishing a gently pitching arch.

[a] Rickard, T. A., The Bendigo gold field: Trans. Am. Inst. Min. Eng., vol. 20, 1892, pp. 538–539.

[b] Faribault, E. R., The gold measures of Nova Scotia and deep mining: Paper read before the Canadian Mining Institute, March, 1899; published by the Mining Society of Nova Scotia, 1899.

[c] Spurr, J. E., Economic geology of the Mercur mining district, Utah: Sixteenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1895, pp. 365–367, 395, 399–401, 449, 454; see also Pls. XXV and XXXIV, and figs. 44 and 45.

No better illustration could be furnished of an impervious pitching arch than that of the Elkhorn mine described by Weed. (See fig. 32.) Here the ore is at the contact of limestone and an overlying argillaceous rock which Weed calls hornstone. The deposit is altogether below the hornstone, and extends down an irregular distance into the limestone which it replaces.[a] It can hardly be doubted that this deposit received its first concentration by ascending waters.

If the criterion that ores in troughs are deposited by descending waters and ores in arches are deposited by ascending waters be applied to the Leadville ore deposits, the conclusion is that the sulphides of Leadville were originally deposited by ascending waters. These ores occur below a relatively impervious porphyry in a much-broken limestone, mainly the Blue limestone.[b] Later, when the second concentration by downward-

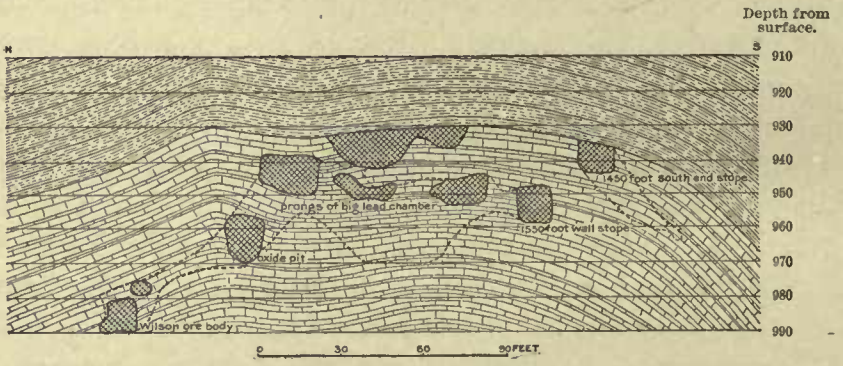

FIG. 32.—Ore deposit in limestone beneath impervious shale, Elkhorn mine, Montana. After Weed.

moving waters occurred, the material which in many places was on denuded anticlines was in part carried down the limbs of the folds under the porphyry into the limestone. At this time, doubtless, also, the limestone was largely dissolved, the ores were carried down, not only along the dip but across the beds, thus producing the very great irregularities which are characteristic of the deposits. If the above explanation be correct, the Leadville ores present another case in which both ascending and descending waters were concerned.[c]

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[a] Weed, W. H., Geology and ore deposits of the Elkhorn mining district, Jefferson County, Montana: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, pp. 472–483.

[b] Emmons, S. F., Geology and mining industry of Leadville, Colo.: Mon. U. S. Geol. Survey, vol. 12, 1886, pp. 539–584.

[c] Blow, A. A., Geology and ore deposits of Iron Hill, Leadville, Colo.: Trans. Am. Inst. Min. Eng., vol. 18, 1890, pp. 173–181.

In this connection it may be suggested that the positions of the ores in reference to the limestone and porphyry in the Leadville district are remarkably similar to those of the ores in the Mercur district in reference to almost identical formations. The forms of the deposits, their irregular under surfaces in the limestone, and the regular surfaces at the porphyry are all identical. Both Emmons and Spurr agree that the ore in the Mercur district was deposited as sulphides by ascending waters. If this be true, the same explanation is probably applicable to the Leadville district.

Another exceedingly interesting illustration of the deposition of ores below an impervious stratum in pitching arches is that furnished by the Enterprise mine of Rico, Colorado, described by Rickard[a] and Ransome.[b] In this district above the ore bodies is an impervious shale, which is very rarely broken by the fissures. The ore occurs in two places: First, ore in nearly vertical fissures extends indefinitely downward below the shale, but not upward into it. The verticals are cut by cross fissures, and where the intersections occur the fissures are likely to be unusually rich. (See p. 1084.) Second, the larger masses of ore are in crushed or fractured limestone below the black shale, but the rich blanket of ore replaces gypsum.[b] These ore bodies are narrow laterally, some being parallel to the strike of the verticals and others parallel to the cross veins. Fig. 29 shows that they occur below anticlinal flexures of the shale made by the deformation resulting in the fracturing and faulting in the more brittle rocks. Rickard regards the deposits as the result of ascending waters, since the fissures continue downward but do not extend upward into the shale. The anticlinal arches have a pitch. Probably the waters issuing from the verticals and the cross fissures followed these arches upward until the pitch somewhere brought them to the surface, at which places the waters escaped as springs, for the waters of the ascending circulation must have somewhere escaped, and that they could not do through the impervious shale.

Porous pitching troughs below, above, or between impervious strata may have different origins from those mentioned. Very frequently such troughs are produced in part or in whole by intrusive igneous rocks. For instance, if an impervious sedimentary stratum has a monoclinal dip and a

[a] Rickard, T. A., The Enterprise mine, Rico, Colo.: Trans. Am. Inst. Min. Eng., vol. 26, pp. 918–973.

[b] Ransome, F. L., The ore deposits of the Rico Mountains, Colorado: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, pp. 254–302.

dike cuts across the stratum, a pitching trough may be produced, as, for instance, in the Penokee-Gogebic district of Michigan and Wisconsin.[a] An intruded igneous rock may follow the contact between folded strata and thus furnish a trough or arch bounded by an impervious formation. Various other ways will occur to one in which pitching troughs or arches with impervious basements, or roofs, or both, may be produced. A trough or arch, no matter how formed, is favorable to the concentration of ores, provided a porous stratum or an opening between the layers furnishes a trunk channel. Of course, other favorable conditions must cooperate with these in order to produce an ore deposit.

Combinations of pervious and impervious strata, united with joints, faults, and other structures which affect some impervious strata and not others, furnish extraordinarily complex sets of conditions which will undoubtedly yield interesting results when studied in special cases.

GENERAL STATEMENTS.

The importance of variation in porosity and structure is sufficiently illustrated in the foregoing pages to show that one of the first steps in studying the genesis of ore deposits formed by aqueous solutions is to investigate the underground circulation. If a geologist wishes to know whether or not adequate supplies of underground water can be obtained for a city, he should at once begin to study the strata, in order to ascertain their varying porosity, their accessibility, the amount of water they carry, their importance as water bearers and water restrainers, and the possible sources of supply; in short, he should make a complete investigation of all of the factors which influence the underground circulation for that district. Frequently this would involve the study of the stratigraphy for extensive areas, often for entire geological provinces. From my own point of view it is equally important, in order to ascertain successfully the genesis of the ore deposits of a given district, to begin by studying the stratigraphy in all its bearings, especially with reference to underground systems of circulation. The problems of stratigraphy and underground circulation being solved, including both the ascending and descending currents, the geologist will have gone far toward the solution of the problem of the genesis of the ores

[a] Irving, R. D., and Van Hise, C. R., The Penokee iron-bearing series of Michigan and Wisconsin: Mon. U. S. Geol. Survey, vol. 19, 1892, pp. 268–275.

for that district. But for some districts not only is it necessary to solve the problem of the present circulation of the underground water, but it is essential that possible past circulations should be studied. Thus, where there are impervious strata which have been largely removed by erosion, the conditions for circulation are very different before and after the removal of the impervious stratum. To illustrate, it has already been pointed out that in various districts in the lead and zinc region of the Mississippi Valley the first concentration took place under conditions of artesian circulation, the upper confining stratum being an impervious shale. Subsequent to that time this shale has been removed from most of the region and a second concentration has taken place by descending water under very different conditions of circulation.

CHARACTER OF TOPOGRAPHY.

EFFECT OF VERTICAL ELEMENT.

Where the relief is marked, the underground circulation is likely to penetrate much deeper than in regions where the variations in relief are slight.

In mountainous and elevated plateau regions the lithosphere is likely to have more numerous, larger, and deeper openings than low-lying areas. Elevated areas are usually those of comparatively recent orogenic or epeirogenic movement. Therefore, they are regions in which the rocks have recently been fractured, and hence the processes of cementation are less likely to have closed the openings. In regions of very steep topography the tendency for the material to glide down the slope under the stress of gravity also tends to widen openings which have been once formed. Such movements are known to be effective to the depth of hundreds of meters. It is hence clear that elevated and rough regions are those in which the underground circulation is likely to find large, numerous, and deep openings. Further, elevated and mountainous regions are those in which the underground water has the greatest difference in head, and this is favorable to deep circulation.

Thus, in mountainous regions, like the Cordilleras, it is to be expected that the underground circulation, both ascending and descending, is effective to greater depths upon the average than in regions of gentle topography. The Cordilleran region is well illustrated by the San Juan

district, where the topography is very rugged. It has been pointed out that oxidizing effects are here produced to a depth of a thousand meters, and it can hardly be doubted that the breadth of the belt of effective ascending circulation is great. In the lead and zinc district of southwestern Wisconsin the topography is gentle, and here the effective circulation, ascending and descending, was confined to a vertical distance of not more than 150 meters; but this is partly due to impervious strata.

EFFECT OF HORIZONTAL ELEMENT.

The horizontal position of an ore deposit with reference to topography often has an important influence upon its richness and magnitude. If the correct theory of circulation of underground waters and the deposition of ores has been given, certain corollaries follow with reference to this point.

(1) Commonly ores deposited by ascending waters should be formed below the valleys, or at least below the lower parts of the slopes; for these are the places where waters are ascending in the trunk channels. (2) Commonly ores deposited by descending waters should be formed below the crests or below the upper slopes of elevations; for these are the places where water would be descending. Probably the upper slopes are more favorable places than the crests; for at an annular belt on the upper slope of an elevation the quantity of descending waters would be greater than at the crests. (3) Commonly ores which receive a first concentration by ascending waters and a second concentration by descending waters should be on the slopes, probably in many instances nearer the valleys than the crests. At such places the meteoric waters falling at the higher elevations have sufficient head to search deeply the zone of fracture for ores. Therefore, the ascending circulation in trunk channels is strong. Further, at such places the level of ground water is a considerable distance below the surface, and abundant descending waters are concentrated in the upper parts of the openings. (See fig. 26, p. 1076.) The downward migration of the belt of weathering furnishes the final favorable condition for the accumulation of a large amount of second concentrates by descending waters.

Admirable illustrations of ore deposits corresponding to the second of the corollaries are furnished by the iron-ore deposits of the Lake Superior region. These are the products of descending waters, and the great majority of the ore deposits are found near the tops of hills or upon the slopes.

For instance, in the Gogebic and Menominee districts of Michigan, where the drainage is across the range, the great ore deposits reach the surface on the slopes or crests, and comparatively little ore has been discovered below the strong cross drainage lines where the waters are probably ascending. All of the great iron-ore deposits reach the surface, but many of them have a pitch which carries them below the rocks. An ore deposit which at the surface starts on a slope or crest may extend below a subordinate cross valley. In such cases the water had head sufficient to carry it down and make it effective below the valley; but, so far as I know, it has yet to be proved that any great deposit continues in force across the valley of an important stream.[a]

The topography in the Mesabi range of Minnesota exerts a somewhat different influence. The productive portion of this range extends from a point west of Hibbing to Embarrass Lake. Here the Giants range to the north is strongly emphasized, and there are good drainage lines to the south. West of Hibbing the Giants range is much less marked; indeed, for much of the distance to the Mississippi River is almost imperceptible.[b] While ore deposits have been discovered in this part of the range, they are not nearly so numerous and extensive as in the area to the east, and the ores which have been found are sandy (indicating an imperfect removal of the silica). There is no known stratigraphic reason why the ore deposits should not have developed as extensively between Hibbing and the Mississippi River as to the east. The only suggestion which has occurred to me in reference to the matter is that because of the dying out of the Giants range and the lack of sufficiently marked elevation and good slopes to produce a vigorous circulation, the groundwater circulation has not been sufficiently vigorous to concentrate the iron oxide and to remove the silica to the same extent as farther east.

An excellent illustration of the third corollary is furnished by the San Juan district of Colorado. In that district the richer parts of the lodes are generally below the middle slopes of the mountains. Nearly all of the great lodes have been opened on veins which outcropped in the so-called "basins" at altitudes of 3,000 to 3,500 meters. Above these basins are the

[a] Van Hise, C. R., The iron-ore deposits of the Lake Superior region: Twenty-first Ann. Rept. U. S. Geol. Survey, pt. 3, 1901, pp. 329–330.

[b] Van Hise, cit., Section on the Mesabi district, by C. K. Leith: pp. 352–353.

high peaks, rising to 4,000 and 4,300 meters. Below the mines are the towns at altitudes from 2,300 to 2,700 meters—that is, the outcrops of the veins are 700 to 1,000 meters above the main valleys.

Another illustration of deposits which are on slopes and are the result of two concentrations is furnished by the lead and zinc district of the upper Mississippi Valley. Chamberlin[a] notes that in the valleys of the Wisconsin part of the district the waters generally ascend to the surface; therefore, at such places only a first concentration would be expected. It is the general impression among miners in this district that a lode makes better on the slope of a hill "than at the summit or at the foot of a hill."[b] Also, it is held by the miners that the lodes which run parallel to a contour of a hill "like an eave trough"[b] are more likely to be rich than those which run toward the summit of the hill. When considered in connection with the topography both of these practical conclusions of the miners are fully explained by the theory of a first concentration by ascending waters and a second concentration by descending waters. This case of the Wisconsin lead and zinc district must not be too strongly insisted upon, for at many places the streams have cut through the lead-bearing limestone into the St. Peters sandstone below, which is a barren formation.

In regions in which there have been recent important changes in the positions of the drainage lines and elevations, the generalizations concerning the relations of ore deposits and topography are only partly applicable. It is well known that in consequence of the varying hardness of rocks, of structure, of the unequal strength of streams and of unequal declivity, drainage lines are almost constantly shifting, in many regions somewhat rapidly. Another way in which the position of the drainage lines with reference to ore deposits may be shifted is by base leveling and subsequent uplift. After a region has been cut down to the level of the sea and is again uplifted it is well known that some of the streams are likely to be along old drainage lines, but that others will be in new positions. It follows that when the second cycle of erosion is well inaugurated an ore deposit which during the first cycle of erosion was in a valley may be on a crest, and vice versa. When it is remembered that there have been various

[a] Chamberlin, T. C., The ore deposits of southwestern Wisconsin: Geology of Wisconsin, vol. 4, 1882, p. 565.

[b] Chamberlin, cit. p. 563.

epochs of extensive base leveling from pre-Cambrian to Tertiary time, it is seen that shifting of drainage lines in consequence of different cycles of topographic erosion may be of great consequence.

Doubtless in consequence of changes in drainage many ore deposits which, when below valleys, received a first concentration by ascending waters, are now well up on slopes or even at crests. A change of this kind is especially favorable to the development of ore deposits which are formed by two concentrations, the first by ascending and the second by descending waters. In an early stage of the history of a deposit it may be in a favorable place to receive a first contribution of ore. Later, if in consequence of a topographic change, it be on higher ground, it is then in a favorable place for the work of descending waters. Although it is difficult to prove, I have little doubt that many ore deposits have had this history.

Where a region has been base leveled it is very difficult to reconstruct the topographic conditions which led to the concentration of the ores. To illustrate, the Lake Superior copper deposits are believed to have been deposited by ascending waters. The waters may have made their way down along fault fractures and through the minor pores to the sloping conglomerate beds and have risen along the beds which had their surface outcrop at a lower elevation than the feeding areas. But all this is purely hypothetical, for the region has been base leveled and the copper deposits unquestionably developed before the end of the base-leveling period. Since that time the region has been uplifted and the present topography incised in the base-leveled plateau. So far as one can see the present topography has no recognizable relation to the ore deposits.

From the foregoing it is apparent that the relation of topography to ore deposits is an important one, and also that in many districts its decipherment is a difficult problem.

PHYSICAL REVOLUTIONS.

The genesis of many ore deposits is undoubtedly further complicated by physical revolutions of various kinds. After an ore deposit has partly formed, either by ascending or descending waters, or both, the region may go through a physical revolution, and after the revolution the concentration of the ores may again be taken up by nature's processes.

After an ore deposit has been formed the country may pass below the level of the sea by denudation and subsidence, may be deeply buried under sedimentary rocks, and may be again uplifted and undergo a second cycle of reactions which affect the nature of the ore deposits. An ore deposit partly formed may be buried deep under volcanic rocks. This undoubtedly has occurred on a great scale in the great region of Tertiary volcanism in the Cordilleras of the West. The ore deposits there buried are placed in a new environment and are undergoing a second cycle of concentration or depletion. In that district it is entirely possible, indeed probable, that ore deposits formed in the pre-Tertiary volcanic rocks, and with a very complex history involving the work of both ascending and descending waters, are now receiving additions of ores from ascending waters, or, on the contrary, are being depleted, and in consequence are contributing metals to waters which are rising. Such waters may deposit the metals in openings within the volcanic rocks, thus making new ore deposits. When in the future denudation shall have stripped off these volcanics, or the upper part of them, these ore deposits will be at the surface. In this connection it is to be remembered that in the Yellowstone Park and other areas there are extensive Tertiary volcanic tuffs in almost every respect like formations which in the San Juan district of Colorado bear important ore deposits, but the San Juan region was so elevated that denudation has thoroughly dissected the volcanic material. Indeed, the major streams have cut down through the volcanics to the sediments below. It may be suggested that when denudation of the volcanic series shall have progressed as far in various other Tertiary volcanic regions as in the San Juan region ore deposits will be exposed, but this may not occur while man occupies the earth.

It is well known that fissures are places of weakness, and that movement has again and again recurred along the old planes. Thus favorable conditions for ore concentration may recur in the same places through various revolutions. Physical changes of various other kinds may take place. Each of the complex changes in physical history produces its effect upon an ore deposit.

V. GENERAL STATEMENTS.

It is clear from the foregoing that an ore deposit may have a wonderfully complex history. It may not represent the work of a single period of ascending or of descending waters, or one cycle of ascending and one cycle of descending waters, but may be the result of a number of cycles of deposition by ascending or descending waters, or both.

Thus irregularities in certain of the ore deposits in very ancient rocks may be explained. But in many cases it appears probable that the main work in an existing ore deposit has been done by continuous concentration, first by ascending waters, second by descending waters, although in such cases part or even all of the metals may have been derived from earlier concentrations.

Any of the special and local factors above discussed and others not considered may in an individual case be so conspicuous as to appear to be a controlling factor in the formation of an ore deposit. One might say that the existence of a given trough was the cause of the production of an ore deposit. The truer statement would be that the factor under consideration is one essential among many. The porosity of a formation, the existence of a pitching trough, favorable topography, the presence of igneous rocks furnishing heat to make the waters active, and many other special factors may, in a given case, all be essential, and without the help of any one of them an ore deposit would not have been produced, but no combination of factors will form an ore body if a source of the metal is not available upon which the underground waters may act. In short, each case of the development of an ore deposit requires the fortunate combination of many favorable factors, working harmoniously together, the absence of any one of which may prevent the concentration of the ore deposit.

VI. ORE SHOOTS.[a]

No fact is better known concerning ore deposits than that they vary in the most remarkable fashion, both in size and richness. Moreover, these variations are both vertical and horizontal. Frequently rich deposits decrease in size or are wholly cut off with extraordinary abruptness. Other equally rich deposits may appear somewhere else on the same level or on another

[a] For a general discussion of ore shoots in fissures, see Penrose, R. A. F., jr., The mining geology of the Cripple Creek district, Colorado: Sixteenth Ann. Rept. U. S. Geol. Survey, pt. 2, 1895, pp. 162–166.

level in an equally strange and apparently inexplicable manner. The ore masses of exceptional richness are generally called ore shoots. Sometimes they are spoken of as pay streaks, at other times as bonanzas, at other times as chimneys. In this paper ore shoot is used as a general term to include all deposits of exceptional richness or size, of whatever origin. At various places in this paper factors have been mentioned which produce ore shoots. However, because of the very great economic importance of ore shoots, it seems to me advisable to consider under one heading some of the more prominent features of ore shoots deposited from aqueous solutions, even at the risk of repetition.

Ore shoots may be grouped into those which are largely due to structural features, to the influence of the wall rocks, and to secondary concentration by descending waters.

One large class of ore shoots may be explained principally by structural features. These structural features may be the varying size of openings, varying complexity of fractures, flexures, intersections of fractures, and later orogenic movements.

A fracture through a mass of rocks is necessarily uneven. Where there are movements, it follows that the walls are not adjusted to each other. Where convex surfaces are opposite each other, a fissure may be represented by a mere seam. Where, on the other hand, two concave surfaces are opposite each other, a widening may occur which in some cases is sufficient to produce a great room. This is beautifully illustrated by the Comstock lode. This lode showed remarkable variations in its width, here being represented by a narrow seam of clay, there by a great bonanza. The story that tells how Fair and Mackay, with persistent courage, drove along a little seam of clay, at places almost unnoticeable, for hundreds of meters, from the 360-meter level of the Gould and Curry mine to the great bonanza, is one of the romances of mining.[a] The clay seam marked a place where two protuberances of the walls had been jammed together so that there was no opening through which circulating waters could pass, whereas the great bonanza represented a place where both walls bowed outward and thus gave ample space for the deposition of the great deposit. Rooms may be produced also partly or largely by solution, and may be connected by comparatively large channels.

[a] Lord, Eliot, Comstock mining and miners: Mon. U. S. Geol. Survey, vol. 4, 1883, pp. 309–314.

It has been shown, other things being equal, that the underground circulation follows the larger openings. Thus the abundant circulation is converged wherever there are rooms, especially where they are connected with passages of considerable width. Moreover, the solutions of such a circulation are likely to be derived from various sources. Hence, upon the average, in the large openings the ore is in greater quantity and very frequently richer than in the narrower ones, where the solutions are both less abundant and less complex.

It is evident from the above that there may be every variation in the width of an ore deposit due to uneven walls, from zero to many feet.

Ore shoots are frequent where the fractures, instead of being simple, are complex; that is, where there is a crushed zone, or zone of brecciation and mashing. It has been pointed out (pp. 1086–1088) that some ore deposits are largely due to reactions between the solutions and the rocks through which they pass. Such an ore deposit is most likely to be rich at a crushed zone, where the interaction between the solutions and the rocks through which they circulate is much greater than at a point where there is a single fracture, even if the latter furnishes a larger space than the multitude of smaller openings. (See pp. 1213–1215.)

The Cripple Creek district is an excellent illustration of a region in which the fracturing is of an extremely complex character. The ores and gangue are largely impregnation and replacement products of the rocks in which they occur, including granite, andesite, phonolite, basalt, etc. The solutions in this district evidently followed the innumerable minute fractures of all kinds and had a very large surface of contact.[a] A condition for the deposition of the ore and gangue was the previous enlargement of the openings by solution.

Very frequently the rich shoots of ore are located by flexures, the ore being either at the crests of anticlines or at the bottoms of synclines. As pointed out (pp. 1206–1212), this is especially likely to be the case where, in connection with the folds, there are impervious strata. Under such conditions, as has already been fully explained, ore is likely to be converged from ascending solutions in the arches of pervious strata below impervious strata, and from descending waters in troughs of pervious strata above impervious strata. In the cases cited, such as those of

[a] Rickard, T. A., The lodes of Cripple Creek: Trans. Am. Inst. Min. Eng., vol. 33, 1903, pp. 613–618.

Australasian and Nova Scotian gold ores and the Lake Superior iron ores, these relations are perfectly clear. Doubtless in many mines there are minor flexures which have been overlooked, but which may be sufficient to control the movement of the circulation, and thus produce the chimneys of ore. These minor flexures may be parallel with the dip of a deposit, or they may pitch to the right or to the left as one looks down the dip.

The intersections of fractures furnish one of the most frequent explanations of ore shoots. The intersections may be those of faulted fissures, those of fissures and joints, or the intersections of joints. In many instances one set of fractures carries the larger ore deposits, and the intersecting set or sets of fractures are known as side fractures. In some instances deposits may occur in two or more sets of intersecting fractures, and in others one of the intersecting sets may be barren of deposits.

In all cases where intersecting fractures occur solutions are contributed from two or more sources. The solutions invariably have different compositions, and therefore precipitation is likely to occur at or near the junctions. In some cases metalliferous material may be furnished by more than one set of fractures, while in other cases it may be contributed by one set of fractures and the precipitating agents by the others. In those instances where the intersecting veins all carry ore it is easy to see why the deposits at the intersections are unusually large and rich. Where the side veins are small or are wholly filled with gangue material their importance in the genesis of ore deposits has been very generally overlooked. In many instances there is little doubt that the metallic material was precipitated in a main fissure at or near the point where the side veins join, through the influence of the solutions contributed by the latter veins. A very clear case of the influence of barren side veins is that already cited of the Enterprise mine, of Rico, Colo., where the pay shoots are especially rich in the main fissures at the places where barren side veins intersect them.

Not infrequently, where a side fracture intersects a vein carrying the main deposit, the high values are not exactly at the intersection, but a little way from it. This is a natural consequence of the laws of circulating waters. Where two streams come together from different sources they are sure to have different heads. If the side fracture which furnishes the precipitating solution has the greater head its water will occupy the main

fissure for some distance on either side of it, the solutions furnished by the main fissure being excluded; but at a greater or less distance from the intersection the solutions from the two sources become mingled and precipitation takes place, thus producing rich ore shoots. This relation is very well illustrated at the Silver Age mine, at Idaho Springs, Colo. Here the ore shoots are connected with intersecting fractures. They are in the main vein at places near, but not directly at intersections of the subordinate fissures. Again, at the Last Dollar mine in the Cripple Creek district the main vein is cut by numerous cross veins, which upon the whole have not been very profitable; but at numerous places the very rich values are found in the main veins comparatively close to the cross veins; that is, at distances from them varying from 15 to 60 meters. Where ore shoots are found to be connected structurally with barren side veins a consideration of the minerals of the main vein and of the side veins ought to lead to more exact knowledge concerning the manner of the precipitation of the metal; for presumably the precipitation of the metals was connected with some of the compounds which occur as gangue, and in the side veins these may be different from those of the main vein.

Side fractures may be at right angles to the main fractures or incline to them. They may extend directly down the dip or pitch to the right or left along the dip. Therefore almost any curious distribution of the rich shoots may occur. All of these relations of fractures with lodes are beautifully illustrated in the San Juan district. Here some fractures strike parallel with the lodes, but dip at considerable angles with them. There are also cross fractures which differ from the lodes both in strike and dip.[a]

Usually side streams bearing either metals or precipitating agents or both do not issue equally all along the faults or joints, but may be largely converged into large channels, and under such circumstances strong springs enter the fissures. Where such springs empty into a room produced by the structural features, discussed on pp. 1224–1225, bonanzas may be formed, such as those of the Comstock lode.

While the relative influence of the different sets of intersecting fractures is very complex, in an individual mine a close study of the number, order, and relations of the fractures and joints, many of which are, perhaps,

[a] Ransome, F. L., A report on the economic geology of the Silverton quadrangle, Colorado: Bull. U. S. Geol. Survey No. 182, 1901, p. 59.

almost imperceptible, may furnish rules which will enable one to more intelligently search for ore.

Between the two cases of trunk channels produced by flexures (described on pp. 1225–1226) and by cross fractures (described on pp. 1226–1228) there are complete gradations.

Late orogenic movements explain certain ore shoots. After openings have received a first contribution of ore, and are, perhaps, fully cemented by ore and gangue materials, orogenic movements frequently recur, which again fracture the ground and produce openings. Some parts of a deposit may escape fracture, while other parts may be broken. The fracturing of the broken parts may be simple or complex. The latter may produce zones of parallel fractures, zones of intersecting fractures, brecciated zones, or even zones in which the material is finely mashed. Between the parts of a deposit where fracturing is absent and those where it is most complex there may be all gradations. The fractures may be confined to a narrow belt of a deposit or to one side of it, and to varying limits laterally or vertically. Entirely new sets of openings may be produced in the wall rock. All of the above statements in reference to a main deposit apply equally well to intersecting deposits. Therefore an ore deposit which has received a first contribution and is subjected again to orogenic movements is in such a condition that it may again receive a contribution of ore material under the same complex laws as at first. The late fractures may be filled with new contributions of metals from the original source; they may be fed by the solution of the deposits before formed; or they may derive metal both from the original source and from the earlier deposit.

The new ore may be distributed very irregularly through the older ore, may be superimposed upon the old material where there are openings, may be deposited as relatively small secondary veins, or any combination of these may take place. The original irregularities in the tenors of the veins, combined with the irregular deposition of the secondary material, may give extraordinary and apparently inexplicable variations in richness. Excellent examples showing how secondary fracture produces very rich subordinate veins are furnished by the San Juan district of Colorado. At the Smuggler Union, deep in the mine, in a secondary fracture adjacent to the main vein, are found extraordinarily rich deposits of free gold in quartz, having an exceedingly irregular and "pockety" distribution of values. It seems probable that in this fracture the gold has been precipi-

tated as a result of reducing solutions furnished by the adjacent sulphides of the main vein. At the famous Camp Bird mine there are thin black seams deep below the surface, which are extraordinarily rich in gold.[a] The main part of the vein has its gold and silver values in copper sulphides, galena, blende, and other base sulphides and in tellurides, but the fine black material in the small veins apparently contains free gold, as is shown by the fact that 75 per cent of the value of the ores is collected on the plates. It seems perfectly clear that these minute seams of rich gold-bearing material are the results of precipitation in secondary fractures.

Ore shoots in many cases are explained by the influence of the wall rocks. It is well known that where ore deposits intersect a complex set of rocks the pay shoots are likely to have a decided preference for one rock. For instance, if a fissure passes from granite to diorite, or from either of these to limestone, or from any of these to sandstone, the character and richness of the deposit may vary greatly as the rock changes. For this variability, due to the character of the wall rocks, different explanations apply in different cases. In some instances the restriction of the ore shoots to one rock is largely explained by its more ready solubility. This is particularly applicable to the substitution deposits, the wall rock being dissolved in advance of or pari-passu with the deposition of the ore. By the solution of the soluble rock sufficient room is furnished for a large ore deposit. The above is undoubtedly the partial explanation in many cases of the occurrence of the ores in limestone rather than in the adjacent more insoluble rocks. Gypsum is even more readily soluble than limestone. Of the Enterprise mine of the Rico district, Ransome[b] says the rich blanket of ore is "due essentially to the removal by solution of a massive bed of gypsum which may have been from 15 to 30 feet [5 to 10 meters] in thickness." All stages of the process of replacement are seen.

In other instances the occurrence of the rich and large bodies with one wall rock rather than with another is due to the fact that the wall rock itself, by reaction upon the solutions, precipitates the ore material. This also partly explains the preference of certain ore deposits for limestone, for, as already explained (pp. 1116–1117), calcium carbonate probably accelerates

[a] Ransome, F. L., A report on the economic geology of the Silverton quadrangle, Colorado: Bull. U. S. Geol. Survey, No. 182, 1901, pp. 89–90.

[b] Ransome, F. L., The ore deposits of the Rico Mountains, Colorado: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, pp. 278–295.

the precipitation of metals as sulphides from their oxidized salts by iron sulphide.

In still other instances the wall rock itself furnishes solutions containing metalliferous material which is precipitated in the trunk channels or furnishes solutions capable of precipitating metalliferous material in the trunk channel. Either of these may be true for igneous rocks. Also igneous wall rocks may furnish heat and thus in a very important measure promote segregation, as explained on pages 1015–1016.

An excellent illustration of the influence of the wall rock is exhibited by the Lake vein of the San Juan district, near Telluride. This vein, profitable in the volcanic tuff, extends through the tuff into the limestones below, and through them into the sandstones. In passing from the tuff into the limestones the vein changes from a quartz vein to a calcite vein, and as it goes into the sandstone it gradually changed again to a quartz vein. There can be no better illustration than this of the influence of the wall rock and of the domination of the law of mass action. The vein material deposited in the limestone and sandstone has essentially the same composition as the rock through which it passes, showing that the minerals deposited in this vein were dependent upon the solutions derived from the adjacent formations. Each formation contributed as its chief material compounds which could be derived from it. Solutions entering the vein from other sources were subordinate to those derived from the wall rock. The influence of the wall rock is further illustrated by the fact that so long as the vein remains in the tuffs it is of economic importance, and as soon as it passes into the sedimentary rocks the amounts of gold and silver become so small that it is valueless.

A third class of ore shoots are those produced by the process which has been so fully explained in this paper, viz, the secondary enrichment of deposits by descending waters, the first concentration of which was produced by ascending waters. This process produces rich ore bodies, either oxidized or sulphureted, or partly each, which are limited in depth by the distance to which the descending waters are effective.

GENERAL STATEMENTS.

Of necessity, in this analysis, the various factors which may produce ore shoots have been separately treated. In a given case it is rare, indeed, to find that the entire explanation lies in the application of a single one of

them. To explain an ore shoot of an individual mine, ordinarily a number of the above causes need to be combined, and in some cases doubtless, other causes which have not been treated. No study is more important economically, more fascinating, or more difficult than to ascertain the particular combination of factors which produced the ore shoots in a given district or mine.

From the foregoing it is plain that no general statement can be made in explanation of ore shoots. In each district, in each mine, in each part of a mine, all the phenomena must be studied closely in the light of correct theories of ore deposition in order to reach an explanation applicable to the particular case.

It is well known that in the districts which are mineralized the workable ore deposits are ordinarily confined to relatively small areas, although, so far as one can see, the amount of metalliferous material furnishing ore deposits may have been the same throughout the districts. The absence of workable ore deposits for the larger parts of the districts ordinarily is due to lack of favorable combination of the various special factors mentioned, and doubtless many others which have not been considered. As better illustrating my meaning, I may again mention the iron and copper ores of the Lake Superior region. The iron-bearing formation has an extensive occurrence through the Lake Superior region, but the workable iron ores are confined to small areas which have been subject to ancient and recent metamorphism, and in which there are favorable structural features. The Lake Superior copper deposits equally well illustrate the principle. All of the mines now being exploited are confined to an exceedingly narrow area on Keweenaw Point, while the copper-bearing rocks occupy an extensive belt about nearly the entire Lake Superior basin. Moreover, these copper-bearing rocks are mineralized in many places, as is shown by the widely disseminated copper. But, unfortunately, in many areas a little copper is concentrated in many amygdaloid or sandstone belts, rather than in a single amygdaloid or sandstone. For instance, in certain districts scores of amygdaloidal flows lie upon one another. In each of these beds the scoriaceous upper surface bears metallic copper, but in none is it in sufficient amount to make the copper a workable deposit. Had the copper deposited in a number of these amygdaloid formations been concentrated in one of them, a workable ore deposit would have been produced.

From the foregoing it is clear that an investigation of the local factors in a district should include both those which are favorable and unfavorable to the concentration of ores, for a study of the latter in many districts may prevent the expenditure of large sums in exploration where the mineralization is general, but the conditions are not such as to have concentrated the valuable material in sufficient quantity at any one position to warrant exploitation.

A treatise on ore deposits, including descriptions of individual districts, necessarily deals with the special factors which are important in each district. These special factors may be considered so conspicuous that the entire attention is given to them. But it is to be remembered that each of these is subordinate to the general principles controlling the deposition of ore deposits in all districts.

SUMMARY AND CONCLUSION.

I shall now make a summary statement of the genetic classification of ore deposits proposed, and consider briefly the relations of these different classes of deposits. It is proposed that ore deposits be divided into three divisions: (A) Sedimentary ores, (B) igneous ores, and (C) metamorphic ores. The sedimentary ores may be divided into two classes: (1) Chemical precipitates, and (2) mechanical concentrates. The mechanical concentrates may be divided into (a) residuary deposits, (b) stream deposits, and (c) beach deposits. As yet criteria have not been formulated by which igneous ores may be subdivided, and therefore there is only one class (1) magmatic segregations. Metamorphic ores are divided into two classes: (1) Gaseous solution ores, and (2) aqueous solution ores. The aqueous solution ores are subdivided into (a) ores deposited by ascending waters, (b) ores deposited by descending waters, and (c) ores deposited by ascending and descending waters combined. The scheme is therefore as follows:

Classification of metallic ore deposits.

- (A) Sedimentary
  - (1) Chemical precipitates.
  - (2) Mechanical concentrates.
    - (a) Residual deposits.
    - (b) Stream deposits.
    - (c) Beach deposits.
- (B) Igneous
  - (1) Magmatic segregations.
- (C) Metamorphic
  - (1) Deposits from gaseous solution.
  - (2) Deposits from aqueous solution.
    - (a) By ascending waters.
    - (b) By descending waters.
    - (c) By ascending and descending waters.

Of the sedimentary ores the important chemical precipitates are those of iron, manganese, and aluminum. Of the mechanical concentrates the residuary deposits include ores of iron and tin; the stream deposits include ores of gold, of tin, and of platinum; the beach deposits include ores of gold and magnetite.

In igneous ores—magmatic segregations—we can only certainly include titaniferous iron ores and the aluminum ores which occur in corundum syenite.

In the metamorphic ores deposited from gaseous solutions are probably to be placed those impregnation deposits associated with which there have contemporaneously developed the heavy anhydrous minerals, such as garnet, wollastonite, amphibole, pyroxene, biotite, and tourmaline. Doubtless many if not all of the ores here belonging developed under the conditions of the zone of flowage or anamorphism. This class is a subordinate one, but includes a number of mines in various districts. Copper seems to be the most important metal of this class, but zinc, lead, gold, silver, etc., occur.

The class of aqueous solution ores is believed to be more important than all others combined. The criteria by which these ores are to be recognized are as follows:

(1) The major portion of the material of the ore deposits, and especially the gangue minerals, is the same as the general cementation materials which fill the openings of rocks of all kinds, from fissures to subcapillary openings. General cementation is universally recognized as the work of aqueous solutions.

(2) The gangue minerals of the ores are dominantly hydrous silicates, carbonates, and oxides, such as are now being produced by aqueous solutions in innumerable localities throughout the world, as, for instance, in the Yellowstone National Park, the Mississippi Valley, Iceland, etc.

(3) At some of these localities in which the gangue minerals are being formed on an extensive scale, metallic ores are also being deposited in small quantities by the aqueous solutions, as at Steamboat Springs, Sulphur Bank, and Boulder Hot Springs.

All of the three subclasses of ores deposited by aqueous solutions are important. Ores of the first subclass, those which at the point of precipitation are deposited by ascending waters alone, comprise ores of gold, silver, and copper, the sulphides of all of the valuable metals, and the tellurides of

gold and silver. This subclass is of very great importance. It is illustrated by the copper ores of the Lake Superior region, by all but the superficial portion of the pyritiferous gold veins of the Sierra Nevada, and by the deposits of many other regions.

The ores which are deposited by descending waters alone are the most important subclass, both as to volume and as to importance to mankind. These ores are chiefly oxides, anhydrous and hydrous. The dominant ores here placed are those of iron. While subordinate amounts of iron ores belong in other divisions, certainly more than 90 per cent and probably more than 95 per cent of the iron ores yet exploited are in this subclass. The ores of manganese also are mainly oxides produced by descending waters.

The ores deposited by ascending and descending waters combined constitute a very important subclass. The materials of this subclass include oxides, carbonates, anhydrous and hydrous silicates, and chlorides, chiefly above the level of ground water; sulphurets and tellurides chiefly below, but often also above it, and native metals both above and below it. There is frequently a transition belt of considerable breadth between the various products. At or near the level of ground water all of these products are often intermingled. Important ores of copper and zinc are included in the oxides; of lead, zinc, and copper in the carbonates; of zinc, copper, and nickel in the hydrous silicates; of silver in the chlorides; of iron, zinc, lead, copper, nickel, mercury, and silver in the sulphides; of gold and silver in the tellurides. The metals include important ores of gold and silver, and subordinate amounts of copper.

It is believed that the ores deposited by ascending and descending waters combined are more numerous than those of any other subclass, even if they do not occur in such great volume and are not of the same importance to man as the ores deposited by descending water alone. I suspect that a close study of the origin of ore deposits will show that of ores formed by underground water the most numerous subclass is not made up of ores deposited by ascending waters alone, but is composed of ores which have undergone a first concentration by this process and a second concentration by descending waters. As a result of this there is found in the upper 50 to 500, or possibly even 1,000, meters of an ore deposit a large portion of the metalliferous material which originally had, as a result of the first concentration, a much wider vertical distribution.

It is to be noted that the ores assigned above to the work of descending waters alone do not include any sulphides. It is by no means asserted that sulphide ores belonging to this subclass do not exist, but I know of no sulphide deposit which can be certainly placed here. If more careful investigation shall show that no important sulphide ores are deposited by descending waters alone it will follow that all aqueous solution sulphide ores belong either to the class deposited by ascending waters or to the class produced by ascending and descending waters combined. It would therefore follow that in the production of all sulphide ores ascending waters are concerned. To my knowledge the only sulphide ores which are held to be the result of descending waters alone are those of the Monte Cristo district of Washington, described by Spurr.[a] But Spurr's statement does not seem to me to prove the conclusion. The mining has extended to only a moderate depth in this district. So far as the facts are known, one might explain the ores as being first concentrated by ascending waters and reconcentrated by descending waters, or as produced by ascending waters alone. It seems to me more probable that the interpretation should be along the line applicable to so many other districts—a first concentration of the sulphides by ascending waters and a later concentration by descending waters.

If the conclusion be established that ascending waters are concerned in the production of all sulphide ores, to this extent the contention of Posepny, who strongly insisted that all sulphide ores are the work of ascending waters, is confirmed. His error would be that he overlooked the importance of the concentrating effect of descending waters. Since the tellurides are so closely associated with the sulphides it is highly probable that they also will be found to be produced not by descending waters alone, but by either ascending waters alone or by ascending and descending waters combined.

To the foregoing classification objections will at once occur. It may be said that there are no sharp dividing lines between the divisions, classes, and subclasses. But transitions are everywhere the law of nature. In a previous chapter (see pp. 786–787, 904–905) I have explained that there are gradations between different classes of rocks, and this statement applies equally well to ore deposits.

[a] Spurr, J. E., The ore deposits of Monte Cristo, Washington: Twenty-second Ann. Rept. U. S. Geol. Survey, pt. 2, 1901, p. 857.

There may be complete gradations between ores deposited by processes of sedimentation and those produced by processes of metamorphism, and between ores apparently most widely separated. Even ores of igneous origin and those deposited by aqueous solutions may grade into each other.

It has been fully explained that ore deposits produced by processes of sedimentation may grade into those produced by processes of metamorphism. Illustrating this, it may be recalled that a placer deposit formed by mechanical concentration may be profoundly modified by the circulating waters of the belt of cementation. Such circulating waters may add greatly to or subtract much from the amount of gold in a mechanical concentration deposit. It is highly probable (as explained on pp. 1042–1043), that the gold conglomerates of the Rand and the deep placers of California have this composite origin. It is also conceivable that ore deposits primarily produced by sedimentation may also be modified by the actions of gaseous solutions, but this is probably much less common than the modification by aqueous solutions.

If it be agreed that ore deposits are produced by magmatic segregation, by gaseous solution, and by aqueous solution, it is certain that a deposit may be partly segregated by one of these processes, and this work supplemented by one or both of the other processes. This may be true of a deposit which is the result of continuous segregation. It is hard to see how an ore deposit produced by magmatic segregation can be formed wholly independent of the action of gaseous and aqueous solutions. If at the time a magma solidifies, magmatic segregation of some valuable metal takes place to a certain extent, after solidification is complete the temperature is still above 365° C. for a considerable time, and the conditions are almost certainly those favorable to the action of gaseous solutions. These may continue the process of segregation for a long time, but finally the temperature falls below 365° C., and then when the temperature is still high and hot water potent, the aqueous solutions begin their work. This work of aqueous solutions may continue to the time the ores are exploited. Thus an ore deposit partly formed by magmatic segregation is sure to be be subsequently modified by the action of gaseous and aqueous solutions. The modification may be by addition or subtraction of the valuable material; that is, in the direction of further enrichment or in the direction of depletion. For the titanic magnetites and the corundum-syenite ores it is not

supposed that the action of the gaseous and aqueous solutions is usually of great consequence; but for the sulphide ores and the gold ores which have been held to be produced by magmatic segregation alone, I hold the work of the solutions to be a necessary and in most instances the dominant part of the process.

Whether ore deposits produced by magmatic segregation are likely to be altered mainly by gaseous solutions or by aqueous solutions will depend largely on the zone in which the igneous rocks are intruded. If the rocks are batholiths in the zone of anamorphism the magmatic segregations which there form are likely to be modified by gaseous solutions, and so long as they remain in that zone aqueous solutions are likely to be unimportant. Where the igneous rocks are intruded into the zone of fracture the conditions are not favorable for action of gaseous solutions for any length of time, but are especially favorable for the long-continued action of aqueous solutions. Thus we would expect that magmatic-segregation ores would be especially likely to be modified by gaseous solutions in the zone of anamorphism, and by aqueous solutions in the zone of fracture.

Metamorphic ore deposits formed mainly by gaseous solutions or by aqueous solutions, or by the two combined, may form without any implication that they are partly due to magmatic processes. Often after igneous rocks are intruded ores do not begin to form until gaseous solutions are active, or much later, when aqueous solutions are at work.

Not only are there transitions between ore deposits produced by sedimentary, igneous, and metamorphic processes, but there are transitions between the classes and subclasses. To illustrate, there are transitions between chemical precipitates and mechanical concentrates; between residual, stream, and beach deposits; between the deposits produced by gaseous and aqueous solutions; between deposits produced by ascending waters, descending waters, and ascending and descending waters.

The chemical precipitates and mechanical concentrates are connected by the residual deposits. Very frequently chemical solution of a rock in which the ore was disseminated is of equal or greater importance than the mechanical concentration. The residual iron ore mantling Iron Mountain, Missouri, is quite as much due to the solution of the porphyry as to its mechanical disintegration. The tin ore in the alluvium of the Malay Peninsula is probably concentrated more extensively by chemical than by

mechanical processes. Thus one might consider that the residual deposits which are classified as mechanical concentrates are partly chemical concentrates, and on this basis chemical deposits might be divided into chemical precipitates and residual concentrates. However, residual deposits are placed with the mechanical concentrates mainly because of their close alliance with stream and beach deposits, which are plainly mechanical concentrates.

This leads to the transition between residual, stream, and beach deposits. It is well known that a residual deposit on a hill or slope may pass by imperceptible stages into the concentrates at the bottom of a stream. It is known also that stream deposits may extend along the stream until the ocean is reached, where a beach deposit may exist. It is therefore clear that there is every possible gradation between residual, stream, and beach deposits.

An ore deposit which is formed mainly by gaseous solutions may be modified by aqueous solutions, for when the temperature has fallen so that the water is below its critical temperature, it is little short of certain that the processes of segregation may and usually will be continued by aqueous solutions, just as in the case of magmatic ores. Thus ore deposits are probably seldom formed solely by gaseous solutions without any subsequent modification by aqueous solutions. Probably very often ore deposits, perhaps inaugurated by precipitation from gaseous solutions, have been profoundly modified by aqueous solutions. Like the ore deposits first segregated by magmatic segregation, the later water action may be in the direction of addition or subtraction. As to the importance of subsequent action by aqueous solutions upon ore deposits partly formed by gaseous solutions, there may be difference of opinion. It is possible that rocks which do not freely permit the circulation of underground water may be more pervious to gaseous solutions, and that in very dense rocks deep within the earth gaseous solutions may segregate ore deposits—such as those associated with heavy anhydrous silicates or gangue minerals—which while in that position are not materially modified by the subsequent action of aqueous solutions. But ore deposits which are formed in the zone of anamorphism must pass well up into the zone of fracture, if not to the surface, before they are accessible to man. They are now in the zone in

which aqueous solutions are active, and while migrating they may be profoundly modified. The amount of subsequent modification, while migrating from the deep zone to the surface, depends upon the conditions of fracture, water circulation, and all the other factors which have been discussed in connection with the deposition of ore deposits by aqueous solutions. The modifications in the zone of fracture of an ore deposit the concentration of which was begun in the zone of flowage, may be, therefore, inappreciable or of dominating importance.

Ore deposits formed by aqueous solutions are not nearly so likely to be modified by gaseous solutions as are the latter by aqueous solutions. Under normal conditions an aqueous ore deposit would not be modified by gaseous solutions, but if there were sufficiently powerful orogenic movements or great igneous intrusions adjacent to an ore deposit partly formed or primarily produced by aqueous solutions, it is conceivable that the water might be raised above its critical temperature and thus a further concentration take place as a result of the work of gaseous solutions. It might be supposed also that an ore deposit partly formed by aqueous solutions might become so deeply buried as to pass into the zone of anamorphism and there be modified by gaseous solutions. Thus, while it is admitted that modification of aqueous solution deposits by gaseous solutions is possible, it is believed that it is exceptional.

Ore deposits which are precipitated almost solely by ascending waters often grade into those in which descending waters have produced an important effect. Thus there is transition between the ores deposited by ascending waters and those deposited by ascending and descending waters. Similarly there is every gradation between ore deposits formed by ascending waters and those produced by descending waters, and between ore deposits formed by descending waters and those precipitated from ascending and descending waters. It may not infrequently happen that a single fissure may fall partly in one subclass and partly in another. Thus a single ore deposit may belong partly in the subclass of ores formed by ascending waters, and partly in the subclass of ores produced by ascending and descending waters. However, most aqueous deposits belong chiefly to one of the three subclasses.

Finally, not only are there gradations between different varieties of the ore deposits among themselves, but there are gradations between the ore

deposits and the rocks, for the ore deposits in many cases are not sharply separated from the country rocks, but grade into them in various ways.

Therefore it appears that not only are there no hard and fast lines between ore deposits of different modes of origin, but that a single ore deposit may be produced by various combinations of most widely diverse processes. Indeed, it is certain that many ore deposits are not produced by a single process, but by several processes, one following another, or even by more than one cycle of processes. Thus, ore deposits which receive the first concentration by magmatic segregation may be concentrated further by gaseous solutions, still further by aqueous solutions, still further by sedimentary processes, and again by aqueous solution. It is clear that there may be every gradation between ore deposits produced solely by magmatic segregation and solely by aqueous solutions.

For the production of many ore deposits in their present condition there have been many stages of concentration by various processes. One cycle of concentration may have followed another through a large part of geological time in accordance with the general law for the segregation of each of the metals in certain formations. (See pp. 947–948.) Many iron-ore deposits have certainly, and many deposits of other metals have probably, been produced as the result of the work of several cycles.

While a part of the metals for many and perhaps most of the ore deposits have an exceedingly composite history, in the majority of cases a final process is dominant, and ore deposits may therefore be fairly classified on the basis of the last permanent process. For instance, there is no question that the Lake Superior iron ores were deposited by descending aqueous solutions; the copper deposits of the same region by ascending aqueous solutions, and the lead and zinc deposits of the Mississippi Valley by ascending and descending aqueous solutions.

Looked at broadly from the above point of view, the total mass of existing ore deposits of all kinds taken together represents the accumulation of the valuable metals of all previous processes of concentration. The processes of segregation are continuous. We catch the series of cycles at a certain stage, and upon the basis of the existing facts we classify them. In coming geological periods existing ore deposits will be sources from which, by various processes of segregation, the ore deposits of that distant time will derive a portion of their material. Another source of

material for such ores will be the igneous rocks which in the future enter the upper part of the lithosphere from the centrosphere.

In conclusion the merits of the classification proposed may be summarized as follows:

First, the classification is strictly genetic, and is based upon a consistent plan.

Second, the primary divisions of metallic ore deposits are parallel with those of rocks. Just as there are sedimentary, igneous, and metamorphic rocks, so there are sedimentary, igneous, and metamorphic ores. If this division of rocks be logical the division of ore deposits is equally logical.

Third, the classification recognizes the gradation and connection between different classes of deposits, one of the most fundamental laws of geology. Recognizing that many ore deposits have a long complex history in which many processes have been concerned, it makes the basis of the classification the last process which resulted in the deposition of the ores where they are now found.

Fourth, it is believed that the classification offered, being strictly genetic and recognizing gradation, is enlightening from a scientific point of view and gives a better idea of the relations of various ore deposits to one another than classifications heretofore proposed.

Fifth, it is believed that the classification will assist mining engineers and geologists in accurately describing deposits, and will give rules to guide them in the exploration and exploitation of ore deposits.

As an illustration of the practical usefulness of the classification is the connection between genesis and depth for those ore deposits in which descending waters were an important factor in concentration. Ores deposited by ascending waters alone are likely to continue to great depth. Therefore, where a given ore deposit has been shown to belong to this class, the expenditure of money for deep exploration may be warranted. Where a deposit is produced by descending waters alone the extent in depth is probably much more limited. In such cases, when the bottom of the oxidized product is reached, it would be folly to expend money in deep exploration with the expectation of finding other rich oxidized masses. Where the ore deposit belongs to the third class, that produced by ascending and descending waters combined, there is a rich upper belt which we can not hope will be duplicated at depth. However, this class of deposit

may grade into the first class, and after the transition the deposit may be rich enough to warrant exploitation at depth. If such work be undertaken, it must be understood that the rich upper products peculiar to the belt of weathering and to the belt of sulphide and telluride enrichment will not be duplicated at depth. It therefore appears to me that the determination to which of the classes of ore deposits produced by underground waters a given deposit belongs has a direct practical bearing upon its exploration and exploitation.

Again it has been seen that the ores produced by magmatic segregation and those which are produced by gaseous solutions form a relatively small class, and not only so, but that the ore deposits themselves are usually rather circumscribed. When, therefore, deposits have either of these origins, experience does not justify the belief that they will be of great importance. For instance, if a copper deposit is associated with heavy anhydrous gangue minerals, and has irregular boundaries, it can not be expected to prove comparable in richness and extent to the great copper deposits produced by aqueous solutions.

It is my hope that mining engineers and geologists will study ore deposits in various regions with reference to the principles discussed in this treatise. It appears to me that he who does this will be capable of interpreting better than before the phenomena which he finds in the ore body or bodies with which he is particularly concerned.

In addition to the points specially emphasized in this volume, accurate descriptions should be made of the relations of the different minerals of ore deposits, of the occurrence of each ore mineral with reference to the wall rocks, and of the variations of the ores in composition and richness at various depths, reckoning both above and below the level of ground water. Moreover, such a study should include close observation of the gangue minerals in their relations to one another and to the valuable minerals, for in many instances they give important testimony as to the origin of the ore deposit. A study should be made of the stratigraphy, including the changes of country rocks and wall rocks, the pervious and impervious formations, the phenomena of deformation, such as folding, faulting, jointing, brecciation, secondary structures, etc. The volcanism of the district should be fully investigated. Finally, the general metamorphism should be worked out. In short, my point of view is that the principles controlling the

deposition of ores must be interpreted in the light of the general principles of geology and especially of metamorphism. It is believed that when a comprehensive study of various ore-bearing districts has been made from this point of view a more satisfactory treatise upon ore deposits may be written than has yet appeared.

Such a study of ore deposits must be a difficult one, involving as it does a working knowledge of stratigraphy, of physical geology in its broadest and most intricate aspects, of petrology, including igneous, sedimentary, and metamorphic rocks, of mineralogy, and of modern physical chemistry. Undoubtedly many ore deposits will be found to be exceedingly complex and not to come fully within the scope of the principles discussed. So far as any ore deposit fails to do this, it will give data upon which to state a more nearly complete theory of ore deposits than that here proposed.

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